

DECLARATION

In the matter of the
Application for Patent under
EPC in the name of TOTO LTD.

I, the undersigned, Kameichi Nakano, of Kyowa Patent
and Law Office located at 2-3, Marunouchi 3-Chome, Chiyoda-
Ku, Tokyo-To, Japan, do solemnly and sincerely declare as
follows:

1. I am well acquainted with the English and
Japanese languages and am competent to translate from
Japanese into English.
2. I have executed to the best of my ability a true
and correct translation into English of the complete
specification and claim(s) originally filed as Japanese
Patent Application No. 182019/1995 dated June 14, 1995.

Dated this 15th day of October, 1997

Kameichi Nakano
Kameichi Nakano

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Title of the Invention: A STAIN-RESISTANT MEMBER AND
APPLICATION TO FORM THEREOF

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Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto CHIKUNI

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Atsushi KITAMURA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Toshiya WATANABE

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Eiichi KOJIMA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto HAYAKAWA

(Translation)

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SPECIFICATION

1. TITLE OF THE INVENTION

A STAIN-RESISTANT MEMBER AND APPLICATION TO FORM THEREOF

2. CLAIMS

1. A stain-resistant member having an exposed surface hydrophilic and a means for maintaining thereof.
2. A stain-resistant member wherein a surface layer having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface.
3. A stain-resistant member according to claims 1 - 2, wherein said means for maintaining an exposed surface hydrophilic is a photocatalyst.
4. A stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance.
5. A stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface.
6. A stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface.

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Applicant:

Identification Number: 000010087

Postal code: 802

Address: 1-1, Nakashima 2-Chome, Kokura-Kita-Ku,
Kitakyushu-Shi, Fukuoka-Ken

Name: TOTO LTD.

Representative: Shigeru Ezoe

Indication of Fee:

Means of Payment: Deposit

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Specification 1

Drawing 1

Abstract 1

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7. A stain-resistance member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface, and an exposed surface is comprised of a hydrophilic substance non-photocatalytic.

8. A stain-resistant member according to claims 5 - 7, wherein an intermediate layer is interleaved between a substrate and a surface layer.

9. A stain-resistant member according to claim 4, wherein said film comprised of a hydrophilic substance is a photo-resistant resin subjected to a hydrophilization process.

10. A stain-resistant member according to claims 6 - 8, wherein said hydrophilic substance non-photocatalytic is a photo-resistant resin subjected to a hydrophilization process.

11. A stain-resistant member according to claims 6 - 8, wherein said hydrophilic substance non-photocatalytic is an inorganic amorphous substance.

12. A stain-resistant member according to claims 5 - 8, wherein said hydrophilic substance is a particle that improves filling of an exposed surface.

13. A stain-resistant member according to claims 5 - 8, wherein said hydrophilic substance is a sintering assistant

of a photocatalytic particle hydrophilic.

14. A stain-resistant member according to claims 9 - 10, wherein said photo-resistant resin subjected to a hydrophilization process is a resin having a Si-O or Si-N bond in a skeleton part.

15. A stain-resistant member according to claims 9 - 10 or 14, wherein said hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a resin wherein at least a skeleton part is comprised of a photo-resistant component.

16. A stain-resistant member having a surface layer comprised of a resin comprised of a photo-resistant component and a photocatalyst, and having a hydrophilic surface simply by light irradiation.

17. A stain-resistant member wherein a photocatalyst is added to a film comprised of a resin comprised of a photo-resistant component, and having a hydrophilic surface simply by light irradiation.

18. A stain-resistant member having a surface layer comprised of a resin having a Si-O or Si-N bond in a skeleton part and a photocatalyst.

19. A stain-resistant member wherein a photocatalyst is added to a film comprised of a resin having a Si-O or Si-N bond in a skeleton part.

20. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, and 18, wherein an electron uptake metal is included in said surface layer.
21. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, and 18, wherein an antibacterial metal is included in said surface layer.
22. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, and 18, wherein silver is included in said surface layer.
23. A stain-resistant member according to claims 4, 9 or 17, and 19, wherein an electron uptake metal is included in said film.
24. A stain-resistant member according to claims 4, 9 or 17, and 19, wherein an antibacterial metal is included in said film.
25. A stain-resistant member according to claims 4, 9 or 17, and 19, wherein silver is included in said film.
26. A stain-resistant member according to claims 8, 10 - 13, and 20 - 22, wherein said intermediate layer is comprised of a thermoplastic binder.
27. A stain-resistant member according to claims 8, 10 - 13, and 20 - 22, wherein said intermediate layer is comprised of glaze.

28. A stain-resistant member according to claims 14 - 16 and 18, wherein said intermediate layer is comprised of a base coat layer comprised of a resin.

29. A stain-resistant member according to claims 8, 10 - 16, 18, and 20 - 22, wherein said substrate is comprised of a substance including an alkali modification component, and said intermediate layer is a layer that prevents diffusion of an alkali modification component.

30. A stain-resistant member according to claims 5, 6, 8, 12, 13, 20 - 22, and 24 - 26, wherein said intermediate layer is formed by a substance with a melting point higher than that of a substrate.

31. A stain-resistant member according to claims 29 and 30, wherein said layer that prevents diffusion of an alkali modification component is a a high purity silica layer.

32. A stain-resistant member according to claims 29 and 30, wherein said layer that prevents diffusion of an alkali modification component is a layer including an electron uptake metal.

33. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 16, 18, 20 - 22, and 26 - 32, wherein a photocatalyst with a thickness exceeding $0.3 \mu\text{m}$ exists over said surface layer.

34. A stain-resistant member according to claims 5 - 8,

10 - 16, 18, 20 - 22, and 26 - 33, wherein the stain-resistant member according to claims 4, 9, 17, 19, and 23 - 25 is stuck or bonded on a substrate surface.

35. An application including a photocatalyst and a photo-resistant resin to form a stain-resistant member according to claims 9, 10, 14 - 25, 28, and 34.

36. A stain-resistant member or an application wherein the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 95% or less, in a stain-resistant member according to claims 9, 10, 14 - 25, 28 and 34, or an application according to claim 35.

37. A stain-resistant member or an application wherein the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 60% or less, in a stain-resistant member according to claims 9, 10, 14 - 25, 28 and 34, or an application according to claim 35.

38. A stain-resistant member providing a UV irradiating means on at least a part of the rim of the stain-resistant member according to claims 1 - 34, or 36 and 37.

39. A stain-resistant member according to claim 38, wherein a UV reflecting means is provided around a UV irradiating means.

40. A stain-resistant member providing a UV irradiating means on the back of the stain-resistant member according to claims 1 - 34, or 36 and 37.

41. A stain-resistant member providing a UV irradiating means on the intermediate layer of the stain-resistant member according to claims 1 - 34, or 36 and 37.

42. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 18, 20 - 22, 26 - 34, and 35 - 41, wherein said substrate is an external wall building material.

43. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 18, 20 - 22, 26 - 34, and 36 - 41, wherein said substrate is a substrate used in a water environment such as a bathtub, washbowl, toilet, and interior tile.

44. A stain-resistant member according to claims 2, 3, 5 - 8, 10 - 18, 20 - 22, 26 - 34, and 36 - 41, wherein said substrate is a floor tile.

45. A stain-resistant member according to claims 1 - 34 and 36 - 44, wherein a contact angle with water on a member surface is 30° or less.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a member having stain-resistance, in a member used in a water environment such as

a bathtub, bathroom inner wall material, bathroom floor material, soap case, bathroom article like a mirror, washbowl, sink, toilet, washing machine, a raincoat and paper diaper; a member used outdoors exposed by rain such as an exterior building material; or a member used under an environment cleaned with water such as a tunnel inner wall material.

[0002]

[Prior Art]

Conventionally, inorganic, plastic, metal, or fiber material, or composite thereof is used for the member used in a water environment or the member used outdoors.

To provide these materials with stain resistance, there are methods of forming a water-repellent resin film on a member surface, and of forming a hydrophilic resin film on a member surface.

[0003]

However, there is a problem that a method of forming a water-repellent resin film like polytetrafluoroethylene on a member surface, leaves fur after water is dried on the member, so that the stain is noticeable.

To solve the problem, recently it has been suggested that hydrophilicity is provided with on the surface of a member used in a water environment or a member used outdoors ("Highpolymer", vol. 44, page 307 (1995)).

[0004]

In other words, a hydrophilic member surface leaves no fur because the surface conforms to water and not to organic stains such oil, even when dirty water including the stains is flown.

[0005]

Conventionally, two methods have been known to render a member surface hydrophilic.

One is to form a member surface with an inorganic amorphous material. The favorable examples are an enamel bathtub, glazed tile, sanitary ware, glass, and mirror.

The other is to form a member surface with a hydrophilic resin such as acrylic, acrylic-styrene ("Highpolymer", vol. 44, page 307 (1995)), polyamide, and polyvinylidene fluoride.

[0006]

[Problems to be Solved by the Invention]

However, both of the conventional methods of rendering a member surface hydrophilic cannot maintain hydrophilicity over a long period.

For example, glass shows a favorable result of a contact angle with water of about 5 - 20° at production; but the glass surface absorbs gradually a polar component such as lower carboxylic acid, being rendered hydrophobic ("Design of Glass Surface", Kindai Henshu-sha (1983)). It is understood that a method of forming with a hydrophilic resin also would produce the same phenomenon. It is an object of the present invention to offer a member that prevents adhesion of organic stains like oil for a long period.

[0007]

[Means to Solve the Problems]

To solve the above problems, the present invention offers a stain-resistant member having an exposed surface hydrophilic and a means for maintaining thereof.

[0008]

In the preferable embodiment of the present invention, a surface layer having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface.

[0009]

In the preferable embodiment of the present invention, the means for maintaining an exposed surface hydrophilic is a photocatalyst.

[0010]

In the preferable embodiment of the present invention, a photocatalyst is added to a film comprised of a hydrophilic substance.

[0011]

In the preferable embodiment of the present invention, a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface.

[0012]

In the preferable embodiment of the present invention, a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface.

[0013]

In the preferable embodiment of the present invention, a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface, and an exposed surface is comprised of a hydrophilic substance non-photocatalytic.

[0014]

In the preferable embodiment of the present invention,

an intermediate layer is interleaved between a substrate and a surface layer.

[0015]

In the preferable embodiment of the present invention, the film comprised of a hydrophilic substance is a photo-resistant resin subjected to a hydrophilization process.

[0016]

In the preferable embodiment of the present invention, the hydrophilic substance non-photocatalytic is a photo-resistant resin subjected to a hydrophilization process.

[0017]

In the preferable embodiment of the present invention, the hydrophilic substance non-photocatalytic is an inorganic amorphous substance.

[0018]

In the preferable embodiment of the present invention, the hydrophilic substance is a particle that improves filling of an exposed surface.

[0019]

In the preferable embodiment of the present invention, the hydrophilic substance is a sintering assistant of a photocatalytic particle hydrophilic.

[0020]

In the preferable embodiment of the present invention, the photo-resistant resin subjected to a hydrophilization process is a resin having a Si-O or Si-N bond in a skeleton part.

[0021]

In the preferable embodiment of the present invention, the hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a resin wherein at least a skeleton part is comprised of a photo-resistant component.

[0022]

In the preferable embodiment of the present invention, a surface layer comprised of a resin comprised of a photo-resistant component and a photocatalyst is provided, and a hydrophilic surface is provided simply by light irradiation.

[0023]

In the preferable embodiment of the present invention, a photocatalyst is added to a film comprised of a resin comprised of a photo-resistant component, and a hydrophilic surface is provided simply by light irradiation.

[0024]

In the preferable embodiment of the present invention, a surface layer comprised of a resin having a Si-O or Si-N bond in a skeleton part and a photocatalyst is provided.

[0025]

In the preferable embodiment of the present invention, a photocatalyst is added to a film comprised of a resin having a Si-O or Si-N bond in a skeleton part.

[0026]

In the preferable embodiment of the present invention, an electron uptake metal is included in the surface layer.

[0027]

In the preferable embodiment of the present invention,

an antibacterial metal is included in the surface layer.

[0028]

In the preferable embodiment of the present invention, silver is included in the surface layer.

[0029]

In the preferable embodiment of the present invention, an electron uptake metal is included in the film.

[0030]

In the preferable embodiment of the present invention, an antibacterial metal is included in the film.

[0031]

In the preferable embodiment of the present invention, silver is included in the film.

[0032]

In the preferable embodiment of the present invention, the intermediate layer is comprised of a thermoplastic binder.

[0033]

In the preferable embodiment of the present invention, the intermediate layer is comprised of glaze.

[0034]

In the preferable embodiment of the present invention, the intermediate layer is comprised of a base coat layer comprised of a resin.

[0035]

In the preferable embodiment of the present invention, the substrate is comprised of a substance including an alkali modification component, and the intermediate layer is a layer that prevents diffusion of an alkali modification component.

[0036]

In the preferable embodiment of the present invention, the intermediate layer is formed by a substance with a melting point higher than that of a substrate.

[0037]

In the preferable embodiment of the present invention, the layer that prevents diffusion of an alkali modification component is a a high purity silica layer.

[0038]

In the preferable embodiment of the present invention, the layer that prevents diffusion of an alkali modification component is a layer including an electron uptake metal.

[0039]

In the preferable embodiment of the present invention, a photocatalyst with a thickness exceeding $0.3 \mu\text{m}$ exists over the surface layer.

[0040]

In the preferable embodiment of the present invention, the film-like stain-resistant member is stuck or bonded on a substrate surface.

[0041]

In the preferable embodiment of the present invention, an application to form a stain-resistant film having said surface layer comprised of a photocatalyst and a photo-resistant resin, is provided.

[0042]

In the preferable embodiment of the present invention, the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 95% or less.

[0043]

In the preferable embodiment of the present invention, the ratio by weight of said photocatalyst versus the sum of said photocatalyst and photo-resistant resin is 5% or more and 60% or less.

[0044]

In the preferable embodiment of the present invention, a UV irradiating means is provided on at least a part of the rim of the stain-resistant member.

[0045]

In the preferable embodiment of the present invention, a UV reflecting means is provided around a UV irradiating means.

[0046]

In the preferable embodiment of the present invention, a UV irradiating means is provided on the back of the stain-resistant member.

[0047]

In the preferable embodiment of the present invention, a UV irradiating means is provided on the intermediate layer of the stain-resistant member.

[0048]

In the preferable embodiment of the present invention, the substrate is an external wall building material.

[0049]

In the preferable embodiment of the present invention, the substrate is a substrate used in a water environment such as a bathtub, washbowl, toilet, and interior tile.

[0050]

In the preferable embodiment of the present invention,

the substrate is a floor tile.

[0051]

In the preferable embodiment of the present invention, a contact angle with water on a member surface is 30° or less.

[0052]

[Effect of the Invention]

An exposed surface hydrophilic and a means for maintaining thereof are provided, to make a member that prevents adhesion of organic stains like oil for a long period.

[0053]

A layer surface having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface, so that the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0054]

A means for maintaining a hydrophilic surface is a photocatalyst, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilic surface can be maintained for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0055]

A photocatalyst is added to a film comprised of a hydrophilic substance, so that only irradiating a UV light

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such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity of the film surface comprised of a hydrophilic substance can be maintained for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0056]

A surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0057]

A surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0058]

A surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic

is formed on a substrate surface, and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, so that only irradiating a UV light such as a sunray and fluorescent lamp allows a polar organic molecule causing hydrophobicity that adheres to a hydrophilic surface to be decomposed immediately, and the hydrophilicity can be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0059]

A intermediate layer is interleaved between a substrate and a surface layer, so that a variety of functions can be added to the intermediate layer.

[0060]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance is a photo-resistant resin rendered hydrophilic, so that the photocatalyst and resin are mixed in a liquid to be applied or molded on the substrate, that is then simply treated at a room temperature to low temperatures of about 300°C to preferably make the above stain-resistant member.

[0061]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance non-photocatalytic is an inorganic amorphous substance, so that a function to maintain the hard stain resistance on the member surface for a long period can preferably be added.

[0062]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface; a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance non-photocatalytic is a particle that improves filling of the exposed surface, so that a surface layer having a function to maintain the stain resistance with more

than constant film strength even at low temperatures wherein the photocatalyst occurs no neck growth, can preferably be added.

[0063]

In a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface; a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface; a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance; or a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance non-photocatalytic is formed on a substrate surface and an exposed surface is comprised of a hydrophilic substance non-photocatalytic, the hydrophilic substance non-photocatalytic is a sintering assistant of a photocatalytic particlehydrophilic to realize sintering of the surface layer at lower temperatures, so that a surface layer having a function to maintain the stain resistance with more than constant film strength by controlling lowered activity due to particle growth of the photocatalytic particle, can preferably be added.

[0064]

A photo-resistant resin rendered hydrophilic is a resin having a Si-O or Si-N bond in a skeleton part, so that preferably the Si-O or Si-N bond has hydrophilicity, and a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin having these bonds in a skeleton part have the most excellent photo resistance in the resins.

[0065]

A hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a resin wherein at least a skeleton part is comprised of a photo-resistant component, so that a hydrophilic surface with a sufficient film strength can easily be formed, unlike the case where a hydrophilic resin such as polyamide and polyvinylidene fluoride is added directly to a member surface.

[0066]

A member having a surface layer comprised of a resin comprised of a photo-resistant component and a photocatalyst, and having a hydrophilic surface only by light irradiation is formed, so that in the case where a member such as an external wall material used in a sunray-irradiated environment or housing facility equipment used in an environment subjected to indoor illumination, a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance. In addition, a component decomposed by UV irradiation should exist until a surface layer is formed, giving flexibility and promoting cross-link.

[0067]

A member wherein a photocatalyst is added to a film comprised of a resin comprised of a photo-resistant component, and having a hydrophilic surface only by light irradiation is formed, so that in the case where a member such as an external wall material used in a sunray-irradiated environment or housing facility equipment used in

an environment subjected to indoor illumination, a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance. In addition, a component decomposed by UV irradiation should exist until a surface layer is formed, giving flexibility and promoting cross-link.

[0068]

A member having a surface layer comprised of a resin having a Si-O or Si-N bond in a skeleton part and a photocatalyst is formed, so that in the case where a member such as an external wall material used in a sunray-irradiated environment or housing facility equipment used in an environment subjected to indoor illumination, a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance.

[0069]

A member wherein a photocatalyst is added to a film comprised of a resin having a Si-O or Si-N bond in a skeleton part is bonded or stuck on an external wall material used in a sunray-irradiated environment or housing facility equipment used in an environment subjected to indoor illumination, so that a UV-reacted site like an alkyl group included in the resin during use in a sunray or indoor illumination with a UV, can be decomposed or oxidized by UV irradiation to provide stain resistance.

[0070]

An electron uptake metal is included in a surface

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layer, so that in addition to the above stain-resistant effect, especially a deodorizing function based on a photocatalytic function improves preferably to a large extent.

[0071]

An antibacterial metal is included in a surface layer, so that in addition to the above stain-resistant effect, the synergistic effect of a photocatalytic function and the antibacterial metal delivers sufficient antibacterial power on a member surface. In addition, in the case where a member is used in a water or rain-exposed environment, addition of the antibacterial metal releases the antibacterial metal in the water, rendering preferably water itself antibacterial.

[0072]

Silver is included in a surface layer, so that the above antibacterial property can preferably be delivered without lowering a hydrophilicity maintaining function by a photocatalyst.

[0073]

An electron uptake metal is included in a film, so that in addition to the above stain-resistant effect, especially a deodorizing function based on a photocatalytic function improves preferably to a large extent.

[0074]

An antibacterial metal is included in a film, so that in addition to the above stain-resistant effect, the synergistic effect of a photocatalytic function and the antibacterial metal delivers sufficient antibacterial power on a member surface. In addition, in the case where a member

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is used in a water or rain-exposed environment, addition of the antibacterial metal releases the antibacterial metal in the water, rendering preferably water itself antibacterial.

[0075]

Silver is included in a film, so that the above antibacterial property can preferably be delivered without lowering a hydrophilicity maintaining function by a photocatalyst.

[0076]

An intermediate layer is comprised of a thermoplastic binder, so that the thermoplastic binder is applied on a substrate, followed by a photocatalyst, and then the substrate is simply heat-treated at temperatures lower than the heat-resistant temperature of the substrate and higher than the softening temperature of the thermoplastic binder, a surface layer having a function to maintain the stain resistance with more than constant film strength, can preferably be added.

[0077]

An intermediate layer is comprised of glaze, so that the texture, decorative property, and excellent chemical stability of the surface can be maintained.

[0078]

An intermediate layer is comprised of a base coat layer comprised of a resin, so that the following 5 effects are provided. First, a substrate and a surface layer can be combined more strongly to improve peel resistance. A film made only of a resin has a film strength higher than that of a film made of a mixture of a resin and a photocatalyst, and has excellent adhesion.

[0079]

Second, improvement of the peel resistance of a film can increase the ratio of the photocatalyst in a surface layer at the same film strength, improving an effect of maintaining hydrophilicity higher.

[0080]

Third, when the effect of maintaining hydrophilicity by a photocatalyst is constant, a photocatalyst can be concentrated on a surface layer, providing a thinner surface layer.

[0081]

Fourth, the resin on a surface layer should have photo-resistance in a highpolymer skeleton part and be a resin to be rendered hydrophilic (resin comprised mainly of a Si-O or Si-N bond), but a resin forming a base coat layer can be selected freely. Therefore, forming a base coat layer with more inexpensive resin, can reduce production cost.

Also, when the thermal expansion coefficient difference between a substrate and a surface layer is different significantly, an elastic resin or a resin having an intermediate thermal expansion coefficient is used to form a base coat layer, any crack at heat treatment can be prevented.

[0082]

Fifth, when a substrate is uneven largely, the surface of it can be smoothed with a base coat layer, providing the following effects.

An outermost surface layer can easily be smoothed. The smooth outermost surface layer allows a light to be

efficiently irradiated on a photocatalyst, delivering an effect of maintaining hydrophilicity more effectively.

Also, a photocatalyst exists over the whole film almost uniformly, so that the effect of maintaining hydrophilicity can be delivered uniformly over the whole surface of the substrate.

[0083]

A substrate is comprised of a substance including an alkali modification component and an intermediate layer is a layer that prevents diffusion of an alkali modification component, so that surface diffusion of the alkali modification component in the substrate can be prevented during producing or using a member, and lowering of a hydrophilicity maintaining function due to adhesion of an alkali metal or alkaline earth metal to a photocatalytic active point can be controlled.

[0084]

An intermediate layer is made of a substance having a melting point higher than that of a substrate, so that in the case where a substrate is made of a low melting point material like soda glass, a surface layer is resistant to be imbedded in a substrate during producing a member, delivering a hydrophilicity maintaining function more efficiently.

[0085]

A layer that prevents diffusion of an alkali modification component is a high purity silica layer, so that, since the self-diffusing coefficient in the high purity silica layer at low temperatures of the alkali modification component is extremely low, surface diffusion

of the alkali modification component in the substrate can be prevented during producing or using a member, and lowering of a hydrophilicity maintaining function due to adhesion of an alkali metal or alkaline earth metal to a photocatalytic active point can be controlled.

[0086]

A layer that prevents diffusion of an alkali modification component is a layer including an electron uptake metal, so that surface diffusion of the alkali modification component in the substrate can be prevented during producing or using a member, and lowering of a hydrophilicity maintaining function due to adhesion of an alkali metal or alkaline earth metal to a photocatalytic active point can be controlled, improving a photocatalytic function. Therefore, a deodorizing function based on a photocatalyst is improved.

[0087]

A photocatalyst with a thickness exceeding $0.3 \mu\text{m}$ exists over the whole surface layer, so that decomposition for an adhered polar organic molecule can preferably be performed immediately.

[0088]

The above film-like stain-resistant member is stuck or bonded on a substrate surface, so that the hydrophilicity can easily be provided on the substrate surface for a long period, to make a member that prevents adhesion of organic stains like oil for a long period.

[0089]

A stain-resistant member having a surface layer comprised of the above photocatalyst and photo-resistant

resin can be made even at low temperatures of 150°C or less, so that application including the photocatalyst and photo-resistant resin, is applied on a substrate like existing housing facility equipment and external wall material, if necessary, with a curing agent or a base coat layer forming agent, and heat-treated thereof with a burner to make a member.

[0090]

In a stain-resistant member having a surface layer comprised of the above photocatalyst and photo-resistant resin, the ratio by weight of said photocatalyst versus the sum of the photocatalyst and photo-resistant resin is 5% or more and 95% or less, so that the member has a hydrophilicity maintaining effect and favorable wear resistance.

This effect is decisively different from conventionally known a deodorizing effect and effect due to direct oxidative-decomposing action of the photocatalyst such as stain resistance of nicotine. In other words, the effect due to direct oxidative-decomposing action of the photocatalyst like a deodorizing effect becomes weak, when the photocatalyst is covered by a binder or resin, or the mixed ratio of the photocatalyst is low. On the contrary, the main part in stain resistance by the hydrophilicity maintaining effect is a hydrophilic surface; to maintain the function, the photocatalyst should oxidatively decomposes only a further adhered polar molecule. Therefore, the effect can be obtained even when the photocatalyst is covered by a binder and resin, and has a small amount of about 5% by weight.

[0091]

In a stain-resistant member having a surface layer comprised of the above photocatalyst and photo-resistant resin, the ratio by weight of said photocatalyst versus the sum of the photocatalyst and photo-resistant resin is 5% or more and 60% or less, so that the member has a hydrophilicity maintaining effect, favorable wear resistance and sufficient hardness.

[0092]

A UV irradiating means is provided on at least a part of the rim of a stain-resistant member, so that a light source is placed thereon more closely compared with an indoor illumination and sunray, irradiating a UV with a higher intensity on the member surface. Therefore, the hydrophilicity maintaining effect can be realized for a shorter time.

[0093]

A UV reflecting means is provided around the UV irradiating means, so that the UV intensity irradiated on a member surface can be improved, realizing the hydrophilicity maintaining effect can be realized for a shorter time.

[0094]

A UV irradiating means is provided on the back of a stain-resistant member, so that a light source is placed thereon more closely compared with an indoor illumination and sunray, irradiating a UV with a higher intensity on the member surface. Therefore, the hydrophilicity maintaining effect can be realized for a shorter time.

Also, the UV irradiating means is a flat light source, so that the flat light source is simply fixed on the back of

the member by sticking, bonding and baking, e.g. at the end of the step, providing the UV irradiating means easily.

[0095]

A UV irradiating means is provided on the intermediate layer of a stain-resistant member, so that a light source is placed thereon more closely compared with an indoor illumination and sunray, irradiating a UV with a higher intensity on the member surface. Therefore, the hydrophilicity maintaining effect can be realized for a shorter time.

Also, the UV irradiating means is a flat light source, so that the flat light source is simply fixed by sticking, bonding and baking, e.g. in the middle of the step, providing the UV irradiating means easily.

[0096]

The above stain-resistant member is applied to an external wall material, so that the hydrophilicity of the surface thereof is maintained to make an external wall material wherein stains can easily be washed off simply by throwing rain or water.

[0097]

The above stain-resistant member is applied to a member used in a water environment such as a bathtub, washbowl, toilet, and interior tile, so that the hydrophilicity of the surface thereof is maintained to make a member that is resistant to stains due to continuous use.

[0098]

The above stain-resistant member is applied to a floor tile, so that the hydrophilicity of the surface thereof is maintained to make a member that is resistant to stains due

to continuous use and to be hard to slide.

[0099]

Rendering a member surface hydrophilic is made to a degree that the contact angle with water is 30° or less, so that the member is resistant to heavy stains.

[0100]

[Embodiment]

The concrete construction of the present invention is explained based on embodiments. An exposed surface hydrophilic is an exposed surface that shows the hydrophilicity to a degree that stains are resistant, and has a contact angle with water of less than 30°, more preferably less than 10°. This is explained concretely below.

Fig. 1 is a diagram using various resins to check the relation between a contact angle with water and stain adhesion.

The contact angle with water was checked with a contact angle measuring instrument; in the stain adhesion, as shown in Fig. 2, a sample was immersed in an artificial bathtub water (warm water mixed with human being's dirt, lard, and soap) for 3 hours to find specific glossiness around a level surface before and after immersion for an evaluating index. The specific glossiness is glossiness after immersion when an initial glossiness before immersion is 1.

According to Fig. 1, the specific glossiness was lowest around a contact angle with water of 70° to be easy to stain adhesion. The specific glossiness is better for the low angle than for the high angle, and showed almost no change for the angle of less than 30°.

It is evident from the above, that a contact angle with water is less than 30°, showing hydrophilicity to a degree that a stain is resistant.

[0101]

The hydrophilic substance refers to a substance that has an extremely low contact angle with water when no component including both of a hydrophilic group like lower carboxylic acid and a hydrophobic group adheres to a surface. Concretely, examples preferably usable include an inorganic crystalline oxide material such as crystalline alumina, zirconia, titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, dibismuth trioxide and tin oxide; an inorganic amorphous material such as glaze and glass; a resin comprised of a Si-O or Si-N bond of a silicon resin and silazane resin; and a resin having a metal-oxygen bond like a Ti-O bond.

[0102]

The means for maintaining an exposed surface hydrophilic refers to a means that can prevent the exposed surface from being rendered hydrophobic, or can recover the hydrophilicity of the exposed surface rendered hydrophobic; for example, a photocatalyst can preferably be used.

[0103]

For example, the following 2 embodiments can be considered for a stain-resistant member having an exposed surface hydrophilic and a means for maintaining thereof.

One is a film-like stain-resistant member comprised of an exposed surface hydrophilic and a means for maintaining thereof.

In this case, when the means for maintaining an exposed

surface hydrophilic is a photocatalyst, the embodiment like Fig. 3 can be considered.

Fig. 3 shows a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance.

[0104]

The other is a stain-resistant member wherein a surface layer having an exposed surface hydrophilic and a means for maintaining thereof is formed on a substrate surface.

In this case, when the means for maintaining an exposed surface hydrophilic is a photocatalyst, for example, Figs. 4 - 6 can be considered.

In Fig. 4, a surface layer is made of a hydrophilic photocatalyst; in Fig. 5, a surface layer is made of a hydrophilic photocatalyst and a hydrophilic substance; and in Fig. 6, a surface layer is made of a photocatalyst and a hydrophilic substance, and an exposed surface is made only of a hydrophilic substance.

[0105]

The photocatalyst refers to a substance that can generate an electron and a hole by light irradiation with less than a constant wavelength, and as a result, produce active oxygen. Examples having hydrophilicity in these substances include titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, dibismuth trioxide and tin oxide.

The irradiated light sources with less than a constant wavelength, are e.g. a sunray, fluorescent lamp, mercury lamp, incandescent lamp, xenon lamp, BLB lamp, metal halide lamp, iron illuminant lamp and germicidal lamp.

[0106]

Any material for the substrate may basically be used; for example, ceramic, pottery material, metal, glass, plastic, decorative plywood, calcium silicate, mortar, steel plate, paper or composite thereof.

[0107]

The particle that improves filling of an exposed surface refers to a particle that, in generation of a gap like an interstice on a substrate surface, has a particle diameter smaller than the gap and bridges the gap.

The generation of a gap like an interstice on a substrate surface includes both of forming and after calcining. Example of the generation of a gap like an interstice on a substrate surface at forming, is e.g. application of a photocatalytic sol or a photocatalytic particle to a substrate.

A mixed particle for particle-size mixing with a photocatalytic sol or a photocatalytic particle, and a particle that bridges a gap by after-application to a substrate, are applied to the particle that improves filling in this case. Example of the generation of a gap like an interstice on a substrate surface after calcining, is e.g. calcining without rendering the surface dense after a photocatalytic sol or a photocatalytic particle is applied to the substrate.

A mixed particle for particle-size mixing with a photocatalytic sol or a photocatalytic particle, and a particle that bridges a gap by after-application to a substrate before or after calcining, are applied to the particle that improves filling in this case.

[0108]

The sintering assistant refers to an assistant added to give more than constant film strength to a surface layer at low temperatures. For example, tin oxide can favorably be used for a titanium oxide sintering assistant. Preferably, a sintering assistant wherein its sintering mechanism depends on steam-condensation should be better; because the assistant is sintered without condensation, being resistant to cracks at production.

[0109]

The photo-resistant resin refers to a good photo-resistant resin, such as a silicon resin, siloxane resin, fluoro resin, and polysilazane resin, that has a photo-resistant bond such as a Si-O, Si-N, C-F, and Si-F bond.

[0110]

The resin comprised of at least a photo-resistant component in a skeleton part, refers to a resin wherein a main bond that is not an end functional group is comprised of a photo-resistant bond such as a Si-O, Si-N, C-F, and Si-F bond.

[0111]

The hydrophilization process refers to a process oxidizing or decomposing a hydrophobic functional group like an alkyl group to change into a hydrophilic functional group such as a hydroxide or carboxyl group. To perform this, there are, e.g. methods of UV irradiation, contacting of an oxidizing agent such as hydrogen peroxide and ozone, and heating.

[0112]

The electron uptake metal refers to a metal such as Pt,

Pd, Ag, Cu, Au, Ni, Co and Fe, that has a low ionization tendency and is easily self-reduced.

[0113]

The antibacterial metal refers to a metal or ion showing an antibacterial action, or a retainer thereof. For example, a metal such as silver, copper and zinc, or ion thereof is retained to zeolite, apatite, calcium phosphate, zirconium phosphate, aluminum phosphate, titania, and zinc oxide.

[0114]

The thermoplastic binder refers to a binder softened by heating. The example is an organic binder such as glaze, glass and polyvinyl alcohol.

[0115]

The base coat layer refers to a resin layer interleaved between a substrate and a surface layer.

[0116]

The substance including an alkali modification component refers to a substance including alkaline metal, alkaline earth metal or ion thereof. The examples are ceramic including alkaline metal, alkaline earth metal or ion thereof in soda glass, soda-lime glass, sheet glass, sintering agent and impurity; and plastic, fiber and metal including alkaline metal, alkaline earth metal or ion thereof in impurity.

[0117]

The layer that prevents diffusion of an alkali modification component refers to a layer that makes the alkaline modification component in the above substrate hard to reach a surface layer; basically any dense layer not

including an alkaline modification component may be used. The examples are a high purity silica layer, resin layer not including an alkaline modification component, metal layer, ceramic layer or composite thereof.

[0118]

The UV light refers to a light such as a sunray, indoor illumination lamp and illumination belonging to a member, that includes a UV. The kind of the light source should include a UV. The examples are a fluorescent lamp, incandescent lamp, UV lamp, xenon lamp, mercury lamp, BLB lamp, and metal halide lamp.

The UV irradiating means refers to an illumination belonging to a member. It is provided so that a light source is placed at a position closer to a member surface, irradiating a UV with a higher intensity thereon.

[0119]

A method of making a stain-resistant member shown in Figs. 3 - 6, is explained. For an antifogging transparent member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermosetting resin (siloxane resin); and the photocatalyst is anatase-form titanium oxide.

The method is comprised of the steps of: adding a siloxane resin to a anatase-form titanium oxide sol to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, putting the liquid into a mold for heat-curing and mold-release to obtain an intermediate member,

and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0120]

[Formula 1]

[0121]

Preferably, the anatase-form titanium oxide sol is sufficiently dispersed in a suspension. For that reason, the anatase-form titanium oxide that has an isoelectric point of pH 6.5, is dispersed under acidic or alkaline conditions. Any dispersing solvent may basically be used, but water and alcohol are safe and easy to use.

[0122]

After the siloxane resin is added to the anatase-form titanium oxide sol, the diluent is added to lower the viscosity of the liquid and make flowing thereof into the mold easy. Therefore, any kind of diluent to reach this aim may be used, but water and alcohol are safe and easy to use. Also, if the viscosity of the liquid is sufficiently low without adding a diluent, the diluent is not necessarily required.

[0123]

The siloxane resin is added to the anatase-form titanium oxide sol, the diluent is added thereto, followed by the curing agent, to make the liquid, so that a liquid to be applied to a substrate can be generated without agglomerating a suspension.

[0124]

For a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermosetting resin (siloxane resin); the photocatalyst is anatase-form titanium oxide; and an electron uptake metal or antibacterial metal is added.

[0125]

In this case, the method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake ion or antibacterial metal ion, further adding thereto a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, putting the liquid into a mold for heat-curing and mold-release to obtain an intermediate member, and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0126]

Solutions including an electron uptake metal ion are: silver lactate, silver nitrate, silver sulfate, silver chlorate, silver fluoride, platinum sulfate, palladium rhodanide, palladium sulfate, aurous chloride, auric chloride, copper sulfate, cuprous acetate, cupric acetate, cupric sulfate, cupric chloride, cupric bromide, cupric nitrate, cupric chlorate, cupric rhodanide, ferrous chloride, ferric chloride, ferrous sulfate, ferric sulfate, ferrous

iodide, ferrous bromide, ferricbromide, ferric oxalate, ferrous acetate, ferric acetate, ferrous chlorate, ferric chlorate, ferrous nitrate, ferric nitrate, ferrous thiosulfate, ferrous rhodanide, ferric rhodanide, cobalt chloride, cobalt sulfate, cobalt iodide, cobalt bromide, cobalt acetate, cobalt chlorate, cobalt nitrate, nickel chloride, nickel sulfate, nickel iodide, nickel bromide, nickel acetate, nickel chlorate, nickel nitrate, nickel rhodanide, zinc chloride, zinc sulfate, zinc iodide, zinc bromide, zinc acetate, zinc nitrate, and zinc chlorate. Such compound solutions of a soluble antibacterial metal are preferable, because a mixing treatment is easy.

[0127]

Solutions including an antibacterial metal ion are: silver lactate, silver nitrate, silver sulfate, cuprous sulfate, silver chlorate, silver fluoride, cuprous acetate, cupric acetate, cupric sulfate, cupric chloride, cupric bromide, cupric nitrate, cupric rhodanide, zinc chloride, zinc sulfate, zinc iodide, zinc bromide, zinc acetate, and zinc nitrate. Such compound solutions of a soluble antibacterial metal are preferable, because a mixing treatment is easy.

[0128]

Any solvent of a solution including an electron uptake metal ion or antibacterial metal ion, may basically be used, but water and alcohol are safe and easy to use. Also, use of the same kind of an anatase-form titanium oxide sol preferably makes a mixing treatment easy.

[0129]

In mixing an anatase-form titanium oxide sol with a

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solution including an electron uptake metal ion or antibacterial metal ion, the pH of the solution including the antibacterial metal ion should be adjusted to be almost equal to the pH of the anatase-form titanium oxide sol; because a change in the pH of the anatase-form titanium oxide sol is small, without damaging remarkably the dispersion of the anatase-form titanium oxide sol in the suspension.

[0130]

After mixing the anatase-form titanium oxide sol with the solution including an electron uptake metal ion or antibacterial metal ion, a UV light may be irradiated on this solution. This allows the antibacterial metal to be photo-reducibly fixed on an anatase-form titanium oxide particle. Then, the electron uptake effect by the electron uptake metal after a photon is decomposed into a hole and an electron by a photocatalyst, can be delivered more effectively, and the electron to be recombined with the hole is lost by the same amount; therefore, a photocatalytic oxidative-decomposing action based on the hole is improved. Also, the released speed of the antibacterial metal ion can be controlled, providing an antibacterial action for a longer period.

[0131]

The most preferable usable examples are platinum, palladium and silver in the electron uptake metal; and silver in the antibacterial metal. Because, they do not change the speed of reaction wherein R part comprised of an alkyl group in a siloxane resin layer is oxidized (to be understood carboxylic oxidization) or decomposed

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(Formula 1).

[0132]

For a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermoplastic resin; and the photocatalyst is anatase-form titanium oxide.

[0133]

In this case, the method is comprised of the steps of: applying anatase-form titanium oxide particles to an injection mold surface, injective-molding with a thermoplastic resin compound to obtain an intermediate member, and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a thermoplastic resin layer exposedly-formed on the surface of the intermediate member (Formula 1).

[0134]

For a stain-resistant member wherein a photocatalyst is added to a film comprised of a hydrophilic substance shown in Fig. 3, one example is explained in the case where the film comprised of a hydrophilic substance is a thermoplastic resin; the photocatalyst is anatase-form titanium oxide; an electron uptake metal or antibacterial metal is added.

[0135]

In this case, the method is comprised of the steps of: applying a solution including an electron uptake metal ion or antibacterial metal ion to anatase-form titanium oxide particles for photo-reducibly fixing to make mixed particles, applying the mixed particles to an injection mold surface, injective-molding with a thermoplastic resin

compound to obtain an intermediate member, and oxidizing (to be understood carboxylic oxidation) or decomposing R part comprised of an alkyl group in a thermoplastic resin layer exposedly-formed on the surface of the intermediate member (Formula 1).

[0136]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface shown in Fig. 4, one example is explained in the case where the substrate is quartz glass; and the hydrophilic photocatalyst is anatase-form titaniumoxide. In this case, the method is comprised of the steps of: applying to a quartz glass the precursor of anatase-form titanium oxide like titanium alkoxide; and calcining thereof.

[0137]

The precursor of anatase-form titanium oxide refers to a substance that is changed into anatase-form titanium oxide after calcining, including an organic titanic salt like titanium alkoxide and an inorganic titanic salt like titanium sulfate. Use of the precursor of these anatase-form titanium oxide allows preferably uniform application on a substrate. Also, after the precursor is changed into amorphous titanium oxide to cover the substrate uniformly, anatase-form titanium oxide crystal is formed, so that an interstice of $0.2 \mu m$ or more is hard to be produced, and when the surface layer thickness is greater than a visible light wavelength, transparency due to scattering is not lost. Therefore, a large amount of a means for maintaining an exposed surface hydrophilic is added to make prevention of rendering hydrophobic more

effectively.

[0138]

A method applying to quartz glass the precursor of anatase-form titanium oxide is explained below by taking an example in the case where titanium tetraethoxide ($(C_2H_5O)_4Ti$), a kind of titanium alkoxide is used for the precursor of the anatase-form titanium oxide.

[0139]

First, a coating solution is made. The coating solution is made by adding a diluent and hydrochloric acid to titanium tetraethoxide. Alcohol such as ethanol and propanol is easy to handle for the diluent. However, water should not be included as much as possible. When a large amount of water is included, hydrolysis of metal alkoxide is promoted extraordinarily, causing a crack.

Hydrochloric is added to prevent an produced crack in after-drying and heat treatment.

[0140]

Next, the coating solution is applied on a substrate. A flow coating method to apply metal alkoxide is easier and preferable. The flow coating is preferably performed in the dry air. The dry air does not mean the air not including moisture at all, but the air with moisture less than that of the general air (atmosphere). When coating in the general air (atmosphere), hydrolysis is promoted too far due to moisture in the air, making film thickness control hard. Also, one retained amount of titanium tetraethoxide is 100 $\mu g/cm^2$ or less by conversion into that of titanium oxide; this is preferable in terms of prevention of a produced crack.

[0141]

After that, an amorphous titanium oxide film is formed by drying in the dry air for 1 - 10 minutes. Obtaining titanium oxide in the these steps is due to the principle shown below. First, titanium tetraethoxide, a start raw material reacts to a trace of moisture in the dry air mainly at flow coating for hydrolysis to generate titanium hydroxide. Further, dehydrating condensation reaction is produced at drying to generate amorphous titanium oxide on the substrate. A titanium oxide particle generated at this time is high purity of the order of some nm; for that reason, it is sintered at low temperatures compared with this titanium oxide.

[0142]

The application obtained from the above method is calcined at 400°C or more, amorphous titanium oxide is crystallized to obtain a stain-resistant member having an anatase-form titanium oxide film that is dense and has hydrophilicity.

[0143]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed on a substrate surface shown in Fig. 4, one example is explained in the case where the substrate is soda glass; and the hydrophilic photocatalyst is anatase-form titanium oxide.

In this case, preferably, the method comprised of the steps of: applying to soda glass the precursor of silica glass like silicon alkoxide, applying thereon the precursor of anatase-form titanium oxide like titanium alkoxide, and calcining thereof.

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[0144]

Preferably, a high purity silica layer is interleaved between a substrate and a surface layer, so that an alkaline component in soda glass is dispersed on the surface, to adhere to the active point of anatase-form titanium oxide, preventing effectively a photocatalytic activation from being lowering.

Such effect is efficient like soda glass, when an alkali metal such as sodium and potassium, and an alkaline earth metal such as magnesium and calcium are included in the substrate.

[0145]

Applying to soda glass the precursor of silica glass like silicon alkoxide is performed below. First, a coating solution is made.

The coating solution is made by adding a diluent, water and hydrochloric acid to silicon alkoxide like tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$).

The water is added to promote hydrolysis, because silicon alkoxide is stable compared with alkoxide, a transition metal such as titanium, and is resistant to hydrolysis.

The coating solution made is heated by adding water; therefore, it should be left for about one hour, before flow coating onto the substrate.

[0146]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is a tile; the hydrophilic photocatalyst is anatase-form titanium

oxide; further tin oxide is added as a particle that fills an exposed surface. In this case, the method is comprised of the steps of: applying to a substrate surface an anatase-form titanium oxide sol, calcining thereof, applying a tin oxide sol to the surface, and drying thereof.

[0147]

Sintering is preferably performed so that lowering of photocatalytic activation due to a lowered specific surface area with particle growth is less; the treatment is made at low temperatures to a degree that a large interstice is hard to be generated with a secondary particle growth, and at high temperatures to a degree that the interstice rate of the surface layer is as low as possible. For example, when using a sol with an average particle diameter of $0.01 \mu\text{m}$ for a start raw material, the treatment is preferably made at about $400 - 900^\circ\text{C}$.

[0148]

In applying a tin oxide sol to the surface, it is preferable to select a tin oxide sol with the average diameter shorter than that of the interstice on the surface layer. To select it, when a titanium oxide sol with an average particle diameter of $0.01 \mu\text{m}$ is used for the above start raw material and calcined at about $400 - 900^\circ\text{C}$, a tin oxide sol with an average diameter shorter than the particle diameter of titanium oxide at a calcining temperature, is used. The particle diameters are less than $0.01 - 0.02 \mu\text{m}$ at 700°C or less, less than $0.04 \mu\text{m}$ at 750°C , less than $0.1 \mu\text{m}$ at 850°C , and less than $0.3 \mu\text{m}$ at 900°C . It is preferable to use a tin oxide sol with an average particle diameter as short as possible in the above range.

[0149]

Drying may be treated at temperatures to a degree that free water is vaporized, i.e. at 100°C or more.

[0150]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is a tile; the hydrophilic photocatalyst is anatase-form titanium oxide; further tin oxide is added as a sintering assistant.

In this case, the method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a tin oxide sol, applying the mixture on a substrate surface, and calcining thereof.

When, for example, a titanium oxide sol with an average particle diameter of 0.01 μm is used for a start raw material, calcining is made at 750°C or more, making the member dense with preferable wear resistance.

[0151]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is quartz glass; the hydrophilic photocatalyst is anatase-form titanium oxide; further an electron uptake metal or antibacterial metal is added.

In this case, the method is comprised of the steps of: applying to a substrate surface the precursor of anatase-form titanium oxide like titanium alkoxide, calcining thereof, applying to the surface a solution including an electron uptake metal ion or antibacterial metal ion, and irradiating a UV light.

[0152]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst is formed, one example is explained in the case where the substrate is soda glass; the hydrophilic photocatalyst is anatase-form titanium oxide; further an electron uptake metal or antibacterial metal is added. In this case, preferably the method is comprised of the steps of: applying to soda glass the precursor of silica glass like silicon alkoxide, applying thereon the precursor of anatase-form titanium oxide like titanium alkoxide, calcining thereof, applying to the surface a solution including an electron uptake metal ion or antibacterial metal ion, and irradiating a UV light.

[0153]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 5, one example is explained in the case where the substrate is aluminum; the hydrophilic photocatalyst is anatase-form titanium oxide; and the hydrophilic substance is a substance wherein a thermosetting resin (siloxane resin) is rendered hydrophilic.

One method in this case is comprised of the steps of: adding a siloxane resin to an anatase-form titanium oxide sol to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on

the surface of the intermediate member by UV light irradiation (Formula 1).

[0154]

Any method of applying a liquid to a substrate surface may basically be used, but a spray coating and roll coating methods are relatively easy.

[0155]

The other method is comprised of the steps of: applying to an aluminum substrate surface a mixture of a siloxane resin with a curing agent to form a base coat layer, adding thereon the siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid to be applied to the substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0156]

The Auger electron spectroscopy results of the element analysis in the cross-sectional direction of the above intermediate member, are shown in Fig. 7 (a) - (c). Nitric acid was used for dispersion of an anatase-form titanium oxide sol, and a heat-curing treatment was made at 150°C. In Fig. 7 (a), Si, C, N and O can be observed on a sample outermost surface; but Ti not. However, as shown in Fig. 7 (b), Ti as well as Si, C, N and O can be observed at 200 nm under the sample outermost surface. At 200 nm under the surface is a layer comprised only of a siloxane resin, and only Si, C and O that are components thereof can be observed

(Fig. 7 (c)). Thus, it is understood that one layer comprised only of a siloxane resin layer is formed on the sample outermost surface of the intermediate member made by the above making method in this way.

R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of this intermediate member by UV light irradiation, is decomposed or oxidized to be rendered hydrophilic by the action of active oxygen generated from anatase-form titanium oxide at about 20 nm under the surface.

[0157]

The UV light refers to a light including a light with a short wavelength to a degree of energy enough to excite an electron from a valence electron band to a conductive band in a substance having a photocatalytic function, so that a light including a light of less than 400 nm is irradiated for anatase-form titanium oxide.

[0158]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 5, one example is explained in the case where the substrate is a resin; the hydrophilic photocatalyst is anatase-form titanium oxide; and the hydrophilic substance is a substance wherein a thermosetting resin (siloxane resin) is rendered hydrophilic.

One method in this case is comprised of the steps of: adding a siloxane resin to an anatase-form titanium oxide sol to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the

diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0159]

The other method is comprised of the steps of: applying to a substrate surface a mixture of a siloxane resin with a curing agent to form a basecoat layer, adding thereon the siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid to be applied to the substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0160]

Heat-curing may be performed at low temperatures of less than 100°C for a long time, or at 100°C or more and at less than the heat-resistant temperatures of the substrate and base coat layer for a short time. In general, on a surface layer, a photocatalyst has a specific gravity greater than that of a resin. Heat-curing at 100°C or more and at less than the heat-resistant temperatures of the substrate and base coat layer is preferable, because a photocatalyst is concentrated on the upper part, so as to shorten the time for decomposing or oxidizing to be rendered hydrophilic R part comprised of an alkyl group in a siloxane

resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation.

[0161]

For a stain-resistant member wherein a surface layer comprised of a hydrophilic photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 5, one example is explained in the case where the substrate is a resin; the hydrophilic photocatalyst is anatase-form titanium oxide; the hydrophilic substance is a substance wherein a thermosetting resin (siloxane resin) is rendered hydrophilic; further an electron uptake metal or antibacterial metal is added.

One method in this case is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an antibacterial metal ion, adding thereto a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0162]

Another method is comprised of the steps of: adding to an anatase-form titanium oxide sol a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof, applying to the surface a solution

including an antibacterial metal ion, irradiating thereon a UV light to obtain an intermediate member, and oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1).

[0163]

Still another method is comprised of the steps of: adding to an anatase-form titanium oxide sol a siloxane resin to make a mixture, diluting the mixture with a solvent to make a diluent, further adding a curing agent to the diluent to make a liquid, applying the liquid to a substrate surface, heat-curing thereof to obtain an intermediate member, oxidizing or decomposing R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation (Formula 1), applying to the surface a solution including an antibacterial metal ion, and irradiating thereon a UV light.

In these 3 methods, a base coat layer may be interleaved.

[0164]

The advantage of the construction in Fig. 5 is that a surface layer can be formed at low temperatures of about 100°C. Therefore, a surface layer can later be formed on ready-made glass, plastic, metal and ceramic with the above method. Also, the same effect can be expected, even when a film in Fig. 3 or an application comprised of a photocatalyst and a photo-resistant resin is stuck on ready-made glass, plastic, metal and ceramic.

[0165]

For a member wherein a surface layer comprised of a photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 6 and an exposed surface is comprised only of a hydrophilic substance, one example is explained in the case where the substrate is aluminum; the hydrophilic substance is glass; and the photocatalyst is anatase-form titanium oxide.

The advantage of the construction in Fig. 6 is that the surface can be made of glass harder than a resin, and an exposed surface is dense even if powder-like matter is used for a start raw material of the photocatalyst. However, when the particle diameter of the powder is too large, it lowers maintaining and recovering effects of a hydrophilic surface by the photocatalyst; thus, the diameter is preferably 0.3 μm or less.

[0166]

One method in this case is comprised of the steps of: applying to a substrate an anatase-form titanium oxide sol, calcining thereof, and applying thereto glass frit for recalcining.

[0167]

The other method is comprised of the steps of: applying to a substrate an anatase-form titanium oxide sol, and applying thereto glass frit for calcining.

[0168]

For a member wherein a surface layer comprised of a photocatalyst and a hydrophilic substance is formed on a substrate surface shown in Fig. 6 and an exposed surface is comprised only of a hydrophilic substance, one example is

explained in the case where the substrate is aluminum; the hydrophilic substance is glass; the photocatalyst is anatase-form titanium oxide; and an electron uptake metal or antibacterial metal is added.

One method in this case is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake metal ion or antibacterial metal ion, applying the mixture to a substrate, calcining thereof, and applying thereto glass frit for recalcining.

[0169]

Another method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake metal ion or antibacterial metal ion, applying the mixture to a glass substrate, and applying thereto glass frit for calcining.

[0170]

Still another method is comprised of the steps of: applying to a substrate an anatase-form titanium oxide sol, calcining thereof, applying thereto glass frit for recalcining to apply to the surface a solution including a metal ion, and irradiating thereon a UV light.

[0171]

Further method is comprised of the steps of: mixing an anatase-form titanium oxide sol with a solution including an electron uptake metal ion or antibacterial metal ion, applying the mixture to a glass substrate, applying thereto glass frit for calcining to apply to the surface a solution including a metal ion, and irradiating thereon a UV light.

[0172]

The light irradiating means can indoor illumination and

sunray, but a light with high UV intensity should be irradiated on a member surface to improve maintaining and recovering effects of hydrophilicity.

For this reason, for example, a means for irradiating a UV light should be provided on the whole rim of the member or part thereof.

Also, in this case, providing a skirt-like reflecting means so that a means for irradiating a UV light is enclosed, can preferably improve the intensity of a UV irradiated on a mirror surface.

[0173]

In another method, a multiple of transparent plates may be stuck together to make a member, and a means for irradiating a UV light may be interleaved between the members. In this case, the means for irradiating a UV light is preferably a flat light source. Such construction can improve the intensity of a UV irradiated on a mirror surface. In such case, a light source is preferably turned OFF during use, but it is safe if turned ON by mistake, because a UV is absorbed by the photocatalyst on a surface layer.

[0174]

The effect of hydrophilicity maintenance of the above member is explained below based on the experiment examples.

(Example 1)

Tetraethoxysilane, 36% hydrochloric acid, pure water and ethanol, are mixed at a ratio by weight of 6 : 2 : 6 : 86, and the mixture was left for one hour. Then, the mixture was applied to soda glass by the flow coating method to obtain an intermediate member P. Further, titanium

tetraethoxide and ethanol were mixed at a ratio by weight of 1 : 9. The 36% hydrochloric acid of 10% by weight versus titanium tetraethoxide, was added to the mixture to make a coating liquid. This coating liquid was applied to the surface of the intermediate member P in the dry air by the flow coating method. The amount of one application was 45 $\mu\text{g}/\text{cm}^2$ by converting into titanium oxide.

After that, the liquid was dried in the dry air for 1 - 10 minutes, further calcined at 500°C to obtain an embodiment sample A.

A 1% silver lactate water solution by weight was applied to the surface of the embodiment sample A, and was subjected to a BLB fluorescent lamp of 20 W at a distance of 20 cm for one minute to obtain an embodiment sample B. Still, the water-absorbed rate of both of the embodiment samples A and B was less than 1%.

[0175]

The contact angle with water and wear resistance in the embodiment samples A and B, for the purposes of comparison, soda glass and the intermediate member P, were evaluated.

The contact angles with water of the samples after making and the samples subjected to a BLB fluorescent lamp for one month, were evaluated with a contact angle measuring instrument.

In the wear-resistant test, slided wearing with a plastic eraser was performed, and changes in an appearance were compared for evaluation. The evaluating references are shown below.

◎ : No change in 40 reciprocated slidings.

○ : 10 or more and less than 40 slidings caused a surface

layer to be scratched and peeled off.

△: 5 or more and less than 10 slidings caused a surface layer to be scratched and peeled off.

×: Less than 5 slidings caused a surface layer to be scratched and peeled off.

[0176]

[Table 1]

[0177]

Because the soda glass substrate is considerably rendered hydrophobic in terms of a contact angle with water of 50°, water droplets were observed apparently. On the contrary, the embodiment samples A and B, and the intermediate member P had a low contact angle with water of about less than 1°, and the surfaces were sufficiently rendered hydrophilic, observing no water droplets.

After being subjected to the BLB fluorescent lamp for one month, the contact angle with water was 53° of the glass substrate, and 49° of the intermediate member P, and the surfaces were considerably rendered hydrophobic, observing water droplets apparently. In contrast with this, the contact angle with water of both of the embodiment samples A and B was low with about less than 1°, showing the maintained hydrophilicity. No water droplets were observed.

[0178]

Next, the recovering effects of hydrophilicity in the embodiment samples A and B, and C made as shown below, were checked.

The embodiment sample C was made in the following manner. After soda-lime glass was washed with 0.1 M

hydrochloric acid in hot water, titanium tetraethoxide and ethanol were mixed at a ratio by weight of 1 : 9. The 36 % hydrochloric acid of 10 % by weight versus titanium tetraethoxide, was added to the mixture to make a coating liquid. This coating liquid was applied to the surface of the soda-lime glass in the dry air by the flow coating method. The amount of one application was $45 \mu\text{g/cm}^2$ by converting into titanium oxide. After that, the liquid was dried in the dry air for 1 - 10 minutes, further calcined at 500°C to obtain a sample.

In the recovering effects of hydrophilicity, the sample surfaces were wiped off with alcohol to improve the contact angle with water on the surface, then subjected to a BLB with 0.5 mW/cm^2 UV output to measure a time-varying change in the contact angle with water.

[0179]

The results are shown in Fig. 8. The contact angles of the samples A - C were all reduced as time elapsed. However, compared with the sample C, the contact angles of the samples A and B were reduced at a dramatic rate, becoming already 0° 30 minutes later.

[0180]

Then, the antibacterial properties of the embodiment sample B and a soda glass substrate, were checked.

They were evaluated with a colon bacillus (*Escherichia coli* W3110 stock).

Glass plates (100 x 100) on which an bacterial liquid of 0.15 ml (10000 - 50000CFU) was dropped, were contacted on the outermost surfaces of the above samples sterilized with 70% ethanol beforehand and, and then were subjected to

irradiation of a white light (3500 lux) for 30 minutes. The bacterial liquid thereon was wiped away with sterilized gauze to be recovered to a physiological salt water of 10 ml. Then, the survival rate of the bacteria was found for an evaluating index. The evaluating indexes are shown below.

- ◎ : The survival rate of the colon bacillus is less than 10%.
- : The survival rate of the colon bacillus is 10% or more and less than 30%.
- △ : The survival rate of the colon bacillus is 30% or more and less than 70%.
- × : The survival rate of the colon bacillus is 70% or more.

As a result, the soda glass substrate showed ×; while the embodiment sample B showed a favorable result of ◎.

[0181]

(Example 2)

A mixture wherein a curing agent was added to a siloxane resin was applied to a transparent acrylic, plastic substrate of 10 cm square and was heat-treated at 150°C to obtain an intermediate member S.

Each of siloxane resins of 5%, 10%, 50% and 80% by weight versus the sum of the titanium oxide solid content and siloxane resin, was added to a nitric acid peptization type suspension of a titanium oxide sol with an average particle diameter of 0.01 μm , was diluted with propanol, and was subjected to a curing agent to obtain a liquid. This liquid was applied to the surface of this intermediate member S for heat-treatment at 150°C to obtain an

intermediate member T.

This intermediate member T was subjected to a BLB lamp of 0.5 mW/cm^2 for desired time to obtain an embodiment sample. Still, the water-absorbed rate of the sample was less than 1 %.

In the embodiment sample and the intermediate member S, the relation between lamp irradiated time and hydrophilic degree, hydrophilicity and maintenance thereof, recovering effect, wear resistance, and surface hardness, were evaluated.

The surface hardness was evaluated with a hardness wherein a member surface was scratched with a pencil with different hardnesses of 6B - 9H to produce scoring.

[0182]

Fig. 9 shows the relation between lamp irradiated time and hydrophilic degree, when the ratio by weight of the titanium oxide solid content versus the titanium oxide solid content and siloxane resin in the surface layer was changed. The contact angle with water of the intermediate member S was not changed, but the contact angles with water of all samples to which 20%, 50%, 90% and 95% by weight were added, were lowered to about 3° by irradiation within 200 hours. Also, the angle of the sample to which 5 % by weight was added, was lowered to about 10° by lamp irradiation for 200 hours. Thus, it was apparent that all the samples show the preferable hydrophilicity.

[0183]

The evaluating results of the wear resistance are shown in Fig. 10. For the purposes of comparison, the sample wherein a surface layer was formed without adding a siloxane

resin was also evaluated. As a result, the ratio by weight of the titanium oxide solid content versus the sum of the titanium oxide solid content and siloxane resin in the surface layer was 95% or less by weight, showing O; and was 90% or less by weight showing O, with favorable results obtained.

[0184]

The evaluated results of the surface hardness are shown in Fig. 11. The ratio by weight of the titanium oxide solid content versus the sum of the titanium oxide solid content and siloxane resin in the surface layer was 90%, showing about 5B, and was 60%, showing H. Thus, the tendency that the hardness was increased with an increase in the siloxane resin, was observed.

[0185]

Using the same method as Example 1, to evaluate the hydrophilicity and maintaining and recovering effects thereof, the ratio by weight of the titanium oxide solid content versus the sum of the titanium oxide solid content and siloxane resin in the surface layer was 50%, and samples subjected to a lamp for 10 hours, were used. As a result, the contact angles with water of the sample immediately after irradiation, and the sample subjected to irradiation for one month, were less than 3° which showed preferable hydrophilicity; it proved that the effect is maintained.

The sample surfaces were wiped off with alcohol to improve the contact angle with water on the surface, then subjected to a BLB with 0.5 mW/cm^2 UV output to measure a time-varying change in the contact angle with water;

irradiation for about one hour lowered the angle from 30° to about 1°.

[0186]

(Example 3)

A mixture wherein a curing agent was added to a siloxane resin was applied to a 10-cm square tile substrate and was heat-treated at 150°C to obtain an intermediate member K.

A siloxane resin of 50 % by weight versus the sum of the titanium oxide solid content and siloxane resin, was added to a solution wherein a nitric acid peptization type suspension of a titanium oxide sol with an average particle diameter of 0.01 μ m, was mixed with a copper acetate solution with pH that was made almost equal to the pH of the titanium oxide sol by nitric acid, was diluted with propanol, and was subjected to a curing agent to obtain a liquid. This liquid was applied to the surface of this intermediate member S for heat-treatment at 150°C to obtain an external wall embodiment member. Still, the ratio by weight of copper versus the titanium oxide in the embodiment member was 2%. The water-absorbed rate of the sample was less than 1%. The obtained sample and the intermediate member K for comparison, were exposed outdoor for a long period, to evaluate a change in a contact angle with water and stain adhesion.

[0187]

The results are shown in Fig. 12. According to the diagram, the contact angle with water was about 3° 2 days later, showing no change even after 6000-hour exposure.

Also, a large amount of stains adhered to the

intermediate member K, but almost no stain on the embodiment sample was observed.

[0188]

(Example 4)

Enamel and a titanium oxide sol were applied to a tile substrate to be calcined at 880A, rendered thereof to a copper acetate solution, dried thereof, and subjected thereof a BLB lamp to obtain an embodiment sample. The obtained sample and a glazed tile for comparison, were exposed outdoor for a long period, to evaluate a change in a contact angle with water and stain adhesion. As a result, 60 days later, a large amount of stains adhered to the glazed tile, but almost no stain on the embodiment sample was observed.

[0189]

[Effect of the Invention]

A member is provided with an exposed surface hydrophilic and a means for maintaining thereof like a photocatalyst, so as to be resistant to organic stains like oil for a long period.

[Brief Description of the Drawings]

Fig. 1

It is a diagram showing the relation between a contact angle with water and stain adhesion.

Fig. 2

It is a diagram showing an evaluating apparatus for stain resistance.

Fig. 3

It is a diagram showing one embodiment of the present

invention.

Fig. 4

It is a diagram showing another embodiment of the present invention.

Fig. 5

It is a diagram showing another embodiment of the present invention.

Fig. 6

It is a diagram showing another embodiment of the present invention.

Fig. 7

It is an Auger electron spectroscopy profile diagram of an intermediate member produced in the producing step of an antifogging transparent member according to the present invention; (a) is a sample outermost surface, (b) is at 20 nm under the sample outermost surface, and (c) is at 200 nm under the sample outermost surface.

Fig. 8

It is a diagram showing the recovering effect of hydrophilicity of the embodiment according to the present invention.

Fig. 9

It is a diagram showing the relation between lamp irradiated time and hydrophilic degree of the embodiment according to the present invention.

Fig. 10

It is a diagram showing the relation between the weight of titanium oxide and wear resistance in the surface layer of the embodiment according to the present invention.

Fig. 11

It is a diagram showing the relation between the weight of titanium oxide and surface hardness in the surface layer of the embodiment according to the present invention.

Fig. 12

It is a diagram showing the result in an outdoor exposure test of the embodiment according to the present invention.

[Explanation of the Reference Numerals]

- 1 ... Sample,
- 2 ... Artificial bathtub water,
- 3 ... Dirt,
- 4 ... Level surface,
- 5 ... Film comprised of a hydrophilic substance,
- 6 ... Photocatalyst,
- 7 ... Substrate,
- 8 ... Layer comprised of a hydrophilic photocatalyst,
- 9 ... Hydrophilic substance non-photocatalytic,
- 10 ... Hydrophilic photocatalyst,
- 11 ... Exposed surface formed by a hydrophilic substance non-photocatalytic

30-10-97

D E C L A R A T I O N

In the matter of the
Application for Patent under
EPC in the name of TOTO LTD.

I, the undersigned, Kameichi Nakano, of Kyowa Patent
and Law Office located at 2-3, Marunouchi 3-Chome, Chiyoda-
Ku, Tokyo-To, Japan, do solemnly and sincerely declare as
follows:

1. I am well acquainted with the English and
Japanese languages and am competent to translate from
Japanese into English.
2. I have executed to the best of my ability a true
and correct translation into English of the complete
specification and claim(s) originally filed as Japanese
Patent Application No. 99425/1995 dated March 20, 1995.

Dated this 15th day of October, 1997

Kameichi Nakano
Kameichi Nakano

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Title of the Invention: A STAIN-RESISTANT FILM, A STAIN-RESISTANT MEMBER FORMED THEREBY, AND METHOD OF MAKING THEREOF

Number of Claim(s): 10

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto CHIKUNI

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Toshiya WATANABE

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto HAYAKAWA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Atsushi KITAMURA

Applicant:

Identification Number: 000010087

Name: TOTO LTD.

Representative: Shigeru Ezoe

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Specification

Drawing 1

Abstract

(Translation)

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SPECIFICATION

1. TITLE OF THE INVENTION

A STAIN-RESISTANT FILM, A STAIN-RESISTANT MEMBER FORMED THEREBY, AND METHOD OF MAKING THEREOF

2. CLAIMS

1. A stain-resistant film comprising: a resin, whose surface is subjected to a hydrophilization process, comprised of a photo-resistant component; and a substance having a photocatalytic function.
2. A stain-resistant film according to claim 1, wherein a contact angle with water is less than 70°.
3. A stain-resistant film according to claim 1, wherein said substance having a photocatalytic function is comprised mainly of an inorganic oxide crystalline material.
4. A stain-resistant film according to claim 1, wherein said substance having a photocatalytic function is comprised of an inorganic oxide crystalline material and a metal having an electronic uptake effect.
5. A stain-resistant film wherein, in the stain-resistant film according to claim 1, the ratio by weight of the substance having a photocatalytic function versus the sum of said photo-resistant resin and substance having a photocatalytic function is more than 5% and less than 95%.

6. A stain-resistant film according to claim 1, wherein said photo-resistant resin is a resin such as a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin, that is comprised mainly of a Si-O or Si-N bond.

7. A stain-resistant film according to claim 1, wherein said hydrophilic process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in said photo-resistant resin.

8. A stain-resistant film wherein the stain-resistant film according to claims 1-7 is fixed through a resin binder layer on a substrate surface.

9. A method of making a stain-resistant member, comprising the steps of: applying on a substrate surface a mixture in which a curing agent is added to a photosetting resin or a thermosetting resin; further applying thereon a liquid obtained by adding to the precursor of a substance having a photocatalytic function the photosetting resin having a skeleton comprised of a photo-resistant component or the thermosetting resin, followed by a diluent, and further the curing agent; curing said photosetting resin or thermosetting resin by heat treatment to obtain a intermediate member; and oxidizing or decomposing for hydrophilization a photosetting resin exposedly-formed on the surface of said intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin.

10. A method of making a stain-resistant member according to claim 9, wherein said heat treatment is performed at 100°C or more and at less than the heat-resistant temperatures of the substrate and thermosetting resin.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a stain-resistant film formed on a substrate used in a water environment, i.e. a bathtub, full-time bath, washbowl, sink, toilet, exterior building material and the surface of part thereof so as to allow them to be utilized preferably.

[0002]

[Prior Art]

Conventionally, stainless metal materials, plastic materials like FRP and ABS, and inorganic materials like enamel, tiles and sanitary ware, have been used in a water environment.

[0003]

However, there is a problem that these materials to which a stained component adheres heavily, involve much cleaning labor. Thus, recently use of water-repellent resins have been suggested to avoid heavy adhesion of a stained component.

[0004]

[Problems to be Solved by the Invention]

However, a water-repellent resin like a fluoro resin is generally soft and is easy to be scratched. There is a disadvantage that, once the surface of it is scratched,

stains deposit outwardly therefrom easily, with strong adhesion. When the part is left for several days, there is a tendency to make the stain adhesion more heavily by bacteria growth.

[0005]

In view of the above facts, an object of the present invention is to offer a stain-resistant film that is rendered resistant to heavy stains, has a sufficient film strength not to be scratched, and avoids bacteria growth.

[0006]

[Means to Solve the Problems]

To solve the above problem, the present invention offers a stain-resistant film comprised of a photo-resistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function.

[0007]

In the preferable embodiment of the present invention, a contact angle with water is less than 70°, more preferably less than 30°.

[0008]

In the preferable embodiment of the present invention, the substance having a photocatalytic function is comprised mainly of an inorganic oxide crystalline material.

[0009]

In the preferable embodiment of the present invention, the substance having a photocatalytic function is comprised of an inorganic oxide crystalline material and a metal having an electronic uptake effect.

[0010]

In the preferable embodiment of the present invention,

the ratio by weight of the substance having a photocatalytic function versus the sum of the photo-resistant resin and substance having a photocatalytic function is more than 5% and less than 95%.

[0011]

In the preferable embodiment of the present invention, the photo-resistant resin is a resin such as a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin, that is comprised mainly of a Si-O or Si-N bond.

[0012]

In the preferable embodiment of the present invention, the hydrophilic process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in the photo-resistant resin.

[0013]

In the preferable embodiment of the present invention, the above stain-resistant film is fixed through a resin binder layer on a substrate surface.

[0014]

A method of making a stain-resistant member of the present invention, is comprised of the steps of: applying on a substrate surface a mixture in which a curing agent is added to a photosetting resin or a thermosetting resin; further applying thereon a liquid obtained by adding to the precursor of a substance having a photocatalytic function the photosetting resin having a skeleton comprised of a photo-resistant component or the thermosetting resin, followed by a diluent, and further the curing agent; curing said photosetting resin or thermosetting resin by heat treatment to obtain a intermediate member; and oxidizing or

decomposing for hydrophilization a photosetting resin exposedly-formed on the surface of the intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin.

[0015]

The above photosetting resin refers to a resin cured by irradiating a light including a UV, to name e.g. a phosphagen resin, epoxy resin and so on.

[0016]

The above thermosetting resin refers to a resin having a property cured by heating, to name a fluororesin, siloxane resin, silane resin, silazane resin, epoxy resin and so on.

[0017]

The above resin having a skeleton comprised of a photo-resistant component, is made of a photo-resistant component in the mainly formed part of a highpolymer chain, to name i.e. a siloxane resin, fluororesin, silane resin, silazane resin and so on.

[0018]

The above precursor of a substance having a photocatalytic function refers to a substance changing into a substance having a photocatalytic function at least after completion of all steps, to name e.g. a sol suspension of a substance having a photocatalytic function.

[0019]

The above hydrophobic surface refers to a surface comprised of a hydrophobic functional group like an alkyl group on a resin surface.

[0020]

The heat treatment of the above making method is

preferably performed at 100°C or more and at less than the heat-resistant temperatures of the substrate and thermosetting resin.

[0021]

[Effect]

A stain-resistant film is comprised of a photoresistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function so as to be rendered resistant to heavy fur and to have a sufficient film strength not to be scratched.

[0022]

Being rendered resistant to heavy fur is because the surface of a stain-resistant film is subjected to a hydrophilization process. This is probably because the surface subjected to a hydrophilization process when used in a water environment, makes a contact angle with a large amount of water in surroundings very low, spreading a droplet uniformly in a thin film form to avoid adhesion of an organic component (such as protein and fat) with many hydrophobic parts of main stain components.

[0023]

However, polyamide and polyvinylidene fluoride, a highpolymer hydrophilic that are broadly known in general, are soft and have a weak film strength for film forming. The point can be solved by being rendering only the surface of a resin with a strong film strength hydrophilic.

[0024]

In that event, addition of a substance having a photocatalytic function can first decompose or oxidize an

organic component hydrophobic on the surface of a resin having a strong film strength simply by irradiating a UV. Therefore, a hydrophilization process can easily be realized. Further, a trace of an absorbed component adhered on the surface rendered hydrophilic, based on a photocatalytic function, can decompose such component, maintaining its hydrophilicity as long as the light is irradiated. At this point, a contact angle with water is about 5° at production, but is different from that of glass whose surface is rendered hydrophobic gradually with use. Second, active oxygen generated from the substance having a photocatalytic function can increase deodorizing and antibacterial effects.

[0025]

Being rendered hydrophilic to a degree that a contact angle with water is less than 70°, more preferably less than 30°, will be resistant to heavy stains.

[0026]

It is understood that the substance having a photocatalytic function is comprised mainly of an inorganic oxide crystalline material so that the surface is rendered resistant to alkali or alkaline earth metal by adding an inorganic oxide crystalline material. In other words, adhesion of alkali or alkaline earth metal on the surface of a substrate, may cause a stain component like fat to react to adhesive alkaline earth metal, to adhere an insoluble soap stain on the surface; but it is thought that this can be prevented effectively.

[0027]

The substance having a photocatalytic function is

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comprised of an inorganic oxide crystalline material and a metal having an electronic uptake effect so as to be resistant to heavy stains. This is because addition of the metal having an electronic uptake effect allows an electron of electrons and holes generated by the substance having a photocatalytic function to be trapped by the metal, decreasing the diminished probability of the holes by reunion with the electrons; whereby the probability that the holes react to oxygen diffused from the air to generate active oxygen is increased, improving the probability that an organic component hydrophobic is decomposed or oxidized at UV irradiation. Further, increasing the probability of generating active oxygen improves deodorizing and antibacterial effects.

[0028]

The ratio by volume of the substance having a photocatalytic function versus the sum of the photoresistant resin and the substance having a photocatalytic function, is more than 5% and less than 95%; an organic component hydrophobic on the surface of a resin having a particularly sufficient film strength and having a strong film strength, can be decomposed or oxidized simply by irradiating a UV for a short time. Therefore, a hydrophilization process can easily be realized. Furthermore, active oxygen generated from the substance having a photocatalytic function can improve deodorizing and antibacterial effects. In other words, the ratio by volume of 5% or less cannot decompose or oxidize the organic component hydrophobic for a short time, while that of 95% or more cannot realize a sufficient film strength.

[0029]

The photo-resistant resin is a resin such as a siloxane resin, silicon resin like a chlorosilane resin, and silazane resin, that is comprised mainly of a Si-O or Si-N bond; preferably the Si-O or Si-N bond has hydrophilicity and has the most excellent photo resistance in resins.

[0030]

The hydrophilization process is a process decomposing or oxidizing by UV irradiation a UV-reacted site like an alkyl group included in a photo-resistant resin so as to make easily a stain-resistant film having a sufficient film strength.

[0031]

The above stain-resistant film is fixed through a resin binder layer on a substrate surface so as to make the film strength stronger.

[0032]

The stain-resistant member is made by the steps of: applying on a substrate surface a mixture in which a curing agent is added to a photosetting resin or a thermosetting resin; further applying thereon a liquid obtained by adding to the precursor of a substance having a photocatalytic function the photosetting resin or the thermosetting resin, followed by a diluent, and further the curing agent; curing said photosetting resin or thermosetting resin by heat treatment to obtain a intermediate member; and oxidizing or decomposing for hydrophilization a photosetting resin exposedly-formed on the surface of the intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin, so that a stain-resistant

member having a surface rendered hydrophilic can easily be obtained.

[0033]

The heat treatment of the above making method is performed at 100°C or more and at less than the heat-resistant temperatures of the substrate and thermosetting resin, whereby a particle comprised of the substance having a photocatalytic function has a specific gravity higher than that of the thermosetting resin, and the particle comprised of the substance having a photocatalytic function is concentrated on the upper part, so as to shorten the time for decomposing or oxidizing for hydrophilization a photosetting resin exposedly-formed on the surface of the intermediate member by UV light irradiation, or the hydrophobic surface in a layer of the thermosetting resin.

[0034]

[Embodiment]

The concrete embodiments of the present invention are explained based on the drawings. Fig. 1 is a diagram showing an embodiment of the present invention, wherein a film comprised of a photo-resistant resin rendered hydrophilic and a substance having a photocatalytic function, is formed through a resin binder layer on a substrate surface.

[0035]

Fig. 2 is a diagram showing another embodiment of the present invention, wherein a film comprised of a photo-resistant resin rendered hydrophilic, a substance having a photocatalytic function, and a metal having an electronic uptake effect, is formed through a resin binder layer on a substrate surface.

[0036]

Any material for the substrate such as ceramic, pottery material, metal, glass, plastic, decorative plywood, calcium silicate, mortar or composite thereof, may basically be used.

[0037]

Any shape of the substrate may be used; for example, a simple shape such as a tile, wall material, board like floor material, spherical, cylindrical, cylindroid, bar, prism and hollow prism; a complex shape such as sanitary ware, washstand, bathtub, sink and accessory thereof, may be included.

[0038]

The photo-resistant resin refers to a good photo-resistant resin, such as a silicon resin, siloxane resin, fluoro resin, and polysilazane resin.

[0039]

The substance having a photocatalytic function refers to a substance that generates an electron and hole by irradiating a light at below a constant wavelength, producing active oxygen. Such substances are titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, dibismuth trioxide, and tin oxide. These substances may be used alone or used together.

[0040]

The inorganic oxide crystalline material refers to an inorganic oxide crystalline material that is crystallized above a degree that the peak is observed for powder X-ray diffraction.

[0041]

The metal having an electronic uptake effect refers to a metal such as Pt, Pd, Au, Ag, Cu, Ni, Fe, Co and Zn, that has a low ionization tendency and is easily self-reduced. A multiple kind metals may be used together.

[0042]

The resin binder layer may be any of a thermosetting resin, photosetting resin or thermal plasticity resin; especially the thermosetting resin or photosetting resin is only applied on the layer to be heat-treated so as to form the layer relatively smooth. Also, selection and use of said resin having a favorable thermal expansion coefficient depending on the kind of a substrate, are preferable because of crack resistance. Further, a colored resin for the layer may be used to thereby be provided with a design.

[0043]

A method of making a stain-resistance member shown in Figs. 1 and 2 is summarized. First, a method of making a stain-resistant member wherein a film comprised of a photo-resistant resin rendered hydrophilic and a substance having a photocatalytic function is formed through a resin binder layer on a substrate surface as shown in Fig. 1, is explained by taking an example in the case where the substrate is an aluminum substrate; the resin binder layer is a thermosetting resin comprised mainly of a siloxane resin; and the substance having a photocatalytic function is anatase-form titanium oxide.

[0044]

In this case, a stain-resistant member can basically be made by the steps of: applying on an aluminum substrate

surface a mixture in which a curing agent is added to a siloxane resin; further applying thereon a liquid obtained by adding to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent, and further the curing agent; curing the siloxane resin by heat treatment to obtain an intermediate member; and oxidizing (Formula 2) or decomposing (Formula 3) for hydrophilization R part (Formula 1) comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of said intermediate member by UV light irradiation.

[0045]

[Formula 1]

[0046]

[Formula 2]

[0047]

[Formula 3]

[0048]

Basically, any method may be used to apply on an aluminum substrate surface a mixture wherein a curing agent is added to a siloxane resin, but spray coating and roll coating are relatively easy.

[0049]

After applying on an aluminum substrate surface a mixture wherein a curing agent is added to a siloxane resin, drying may be inserted before further applying thereon a liquid obtained by adding to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent, and

further the curing agent. This makes the substrate surface smooth at applying said liquid, applying the liquid more uniformly.

[0050]

The anatase-form titanium oxide sol dispersed sufficiently in a suspension is preferable. For that reason, the anatase-form titanium oxide with a PH 6.5 electric point, is dispersed by under acidic or alkaline conditions. In this case, to improve its dispersion, a finishing activator, a dispersing agent (deflocculant), or a finishing agent, may be added. Any solvent to disperse the anatase-form titanium oxide sol may basically be used. In general, water or ethanol is often used.

[0051]

The siloxane resin is added to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent so as to lower the viscosity of the liquid to easily be applied on the substrate. Any diluent to reach this purpose may basically be used. For example, ethanol, propanol or water can preferably be used.

[0052]

The liquid is made in the order of adding to an anatase-form titanium oxide sol suspension the siloxane resin, followed by a diluent, further the curing agent, whereby the liquid to be applied on the substrate can be generated without agglomerating the suspension.

[0053]

Any method of applying the liquid on the substrate may basically be used, but spray coating and roll coating are relatively easy.

[0054]

The heat treatment may be performed at low temperatures of less than 100°C for a long time, but may preferably be performed at 100°C or more and at less than the heat resistant temperatures of the substrate and thermosetting resin for a short time. In general, a particle comprised of a substance having a photocatalytic function has a specific gravity greater than that of a thermosetting resin. The heat treatment at 100°C or more and at less than heat resistant temperatures of the substrate and thermosetting resin is preferable, because the particle comprised of a substance having a photocatalytic function is concentrated on the upper part, so as to shorten the time for decomposing or oxidizing for hydrophilization R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation.

[0055]

The Auger electron spectroscopy results of the element analysis in the cross-sectional direction of the above intermediate member, are shown in Fig. 3 (a) - (c). Nitric acid was used for suspending an anatase-form titanium oxide sol, and a heat treatment was performed at 150°C.

[0056]

In Fig. 3 (a), Si, C, N and O can be observed on a sample outermost surface, but Ti not. However, as shown in Fig. 3 (b), Ti as well as Si, C, N and O can be observed at 20 nm under the sample outermost surface. As shown in Fig. 3 (c), at 200 nm under the surface is a layer comprised only of a siloxane resin, and only Si, C and O that are

components thereof can be observed. Thus, it is considered that one layer comprised only of a siloxane resin is formed on the sample outermost surface of the intermediate member.

[0057]

R part comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of the intermediate member by UV light irradiation, is decomposed or oxidized for hydrophilization by the action of active oxygen generated from anatase-form titanium oxide at about 20 nm under the surface.

[0058]

The UV light refers to a light including a light with a short wavelength to a degree of energy enough to excite an electron from a valence electron band to a conductive band in a substance having a photocatalytic function, so that a light including a light of less than 400 nm is irradiated for anatase-form titanium oxide.

[0059]

Next, a method of making a stain-resistant member wherein a film comprised of a photo-resistant resin rendered hydrophilic, a substance having a photocatalytic function, and a metal having an electron uptake effect is formed through a resin binder layer on a substrate surface as shown in Fig. 2, is explained by taking an example in the case where the substrate is an aluminum substrate; the resin binder layer is a thermosetting resin comprised mainly of a siloxane resin; the substance having a photocatalytic function is anatase-form titanium oxide; and the metal having an electron uptake effect is copper.

[0060]

In this case, a stain-resistant member can basically be made by the steps of: applying on an aluminum substrate surface a mixture in which a curing agent is added to a siloxane resin; further applying thereon a liquid obtained by mixing an anatase-form titanium oxide sol suspension with a solution including a copper ion, and adding to the mixture a siloxane resin, followed by a diluent, and further the curing agent; curing the siloxane resin by heat treatment to obtain an intermediate member; and decomposing or oxidizing for hydrophilization R part (Fig. 3) comprised of an alkyl group in a siloxane resin layer exposedly-formed on the surface of said intermediate surface by UV light irradiation.

[0061]

A soluble, copper compound solution such as cupric acetate and cupric sulfate can preferably be used for the solution including a copper ion. In the case of a metal having an electron uptake effect, other than copper, a soluble solution such as silver nitrate, silver sulfate, silver lactate, and silver acetate is preferable for making a mixing treatment easy. Also, a solvent such as water, ethanol and propanol can be used for the solution including a copper ion, but the same kind of anatase-form titanium oxide sol suspension is preferable, where possible.

[0062]

In mixing an anatase-form titanium oxide sol suspension with a solution including a copper ion, the PH of the solution including a cooper ion should be adjusted almost equal to the PH of the anatase-form titanium oxide

suspension; because a change in the PH of the anatase-form titanium oxide sol suspension is small, damaging remarkably no dispersion of the anatase-form titanium oxide sol in the suspension.

[0063]

After mixing an anatase-form titanium oxide sol suspension with a solution including a copper ion, a UV light may be irradiated on this solution. This allows copper to be photo-reducibly fixed on the anatase-form titanium oxide particle, promoting a hydrophilization process at a smaller amount of copper.

[0064]

The effect of the above embodiment is explained below based on concrete evaluating experiments.

(Evaluating experiment 1)

First, a variety of resins were used to check the relation between a contact angle with water and stain adhesion. The contact angle with water was measured with a contact angle measuring instrument. For the stain adhesion, as shown in Fig. 4, a sample 6 was immersed in an artificial bathtub 7 (warm water mixed with human being's dirt, lard, and soap) for 3 hours. the specific glossinesses around a level surface before and after immersion were obtained for an evaluating index.

[0065]

The specific glossiness refers to a immersion glossiness when the initial glossiness before immersion is 1.

[0066]

The results are shown in Fig. 5. In the diagram, the

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specific glossiness was the lowest at a contact angle with water of around 70° and was easy to adhere stains. The specific glossiness was improved more in a decrease in the contact angle with water than in an increase in the contact angle, and was almost unchanged at less than 30°.

According to the above, it was evident that a contact angle with water of less than 70°, more preferably at less than 30° makes stain resistance.

[0067]

(Evaluating experiment 2)

About 3 μm of a mixture in which a curing agent was added to the siloxane resin, was applied on a 10 cm square aluminum substrate, and then was heat-treated at 150°C to obtain an intermediate member C. A BLB lamp was irradiated on this intermediate member for 5 days to obtain a comparing sample A.

[0068]

A liquid obtained by adding the siloxane resin to a liquid in which a nitrate-dispersed liquid of a titanium oxide sol with a 0.01 μm average particle diameter was mixed with a 3% copper acetate water solution by weight (the ratio by weight of the titanium oxide versus siloxane resin is 1 : 1), and by diluting with propanol to further add a curing agent, was applied on the surface of the above intermediate member C, and then was heat-treated at 150°C to obtain an intermediate member. The BLB lamp was irradiated on this intermediate member D for 5 days to obtain an embodiment sample B.

[0069]

The contact angles with water for these samples A and

B, and intermediate members C and D, were measured with a contact angle measuring instrument. The results are shown in Table 1. According to the table, the contact angle with water was at a high 70° in the comparing sample A, while the angle was a low 40° in the intermediate member D with which titanium oxide was mixed. Further, the embodiment sample B subjected to a hydrophilization process by irradiating a BLB lamp, was sufficiently rendered hydrophilic with the angle of 3°.

[0070]

Table 1

[0071]

The stain adhesion for the embodiment sample B obtained here, was tested with the same method as the evaluating experiment 1. As a result, a change in the specific glossiness was less than 1%, showing a favorable result.

[0072]

Further, the antibacterial properties of the samples A and B, and intermediate members C and D, were evaluated. They were evaluated with a colon bacillus (*Escherichia coli* W3110 stock). Glass plates (100 x 100) on which an bacterial liquid of 0.15 ml (10000 - 50000CFU) was dropped, were contacted on the outermost surfaces of the above samples and intermediate members sterilized with 70% ethanol beforehand, and then were subjected to irradiation of a white light (3500 lux) for 30 minutes. The bacterial liquid thereon was wiped away with sterilized gauze to be recovered to a physiological salt water of 10 ml. Then, the survival rate of the bacteria was found for an evaluating

index. The evaluating indexes are shown below.

+++ : The survival rate of the colon bacillus is less than 10%.

++ : The survival rate of the colon bacillus is 10% or more and less than 30%.

+ : The survival rate of the colon bacillus is 30% or more and less than 70%.

- : The survival rate of the colon bacillus is 70% or more.

As a result, the intermediate member C and the comparing sample A showed -, while the intermediate member D and the embodiment sample B showed a favorable result of +++.

[0073]

Further, the deodorizing properties of the samples A and B, and the intermediate members C and D, were evaluated. They were evaluated by measuring R30 (L). The R30 (L) refers to the removed rate of an odor component after light irradiation. Concretely, the rate can be obtained by placing 8 cm away from a light source (BLB lamp 4W) a surface in a 11L glass vessel on which a stain-resistant film of each of the samples or members was formed, by filling methylmercaptan gas into the vessel such that the gas has an initial concentration of 3 ppm, and measuring a change in the concentration for 30-minute light irradiation.

[0074]

The R30 (L) value was less than 10% in the intermediate member C and the comparing sample A; while the value was 80% or more in both of the intermediate member D and the embodiment sample B, showing a favorable result.

[0075]

(Evaluating experiment 3)

About 3 μm of a mixture in which a curing agent was added to the siloxane resin, was applied on a 10-cm square aluminum substrate, and then was heat-treated at 150°C to obtain an intermediate member. A liquid obtained by adding the siloxane resin with the ratio by weight of the titanium oxide versus the siloxane resin changed, to a liquid in which a nitrate-dispersed liquid of a titanium oxide sol with a 0.01 μm average particle diameter was mixed with a 3% copper acetate water solution by weight, and by diluting with propanol to further add a curing agent, was applied on the surface of this intermediate member, and then was heat-treated at 150°C to obtain an intermediate member. The BLB lamp was irradiated on this intermediate member D for 5 days to obtain an embodiment sample. Contact angle measurement and a wear-resistant test were conducted for the obtained sample.

[0076]

In the wear-resistant test, slided wearing with a plastic eraser was performed, and changes in an appearance were compared for evaluation. The evaluating references are shown below.

◎: No change in 40 slidings.

○: 10 or more and less than 40 slidings caused a stain-resistant film to be scratched and peeled off.

△: 5 or more and less than 10 slidings caused a stain-resistant film to be scratched and peeled off.

×: Less than 5 slidings caused a stain-resistant film to be scratched and peeled off. The results are shown Fig. 6.

According to the diagram, when the weight of the titanium oxide in the stain-resistant film is less than 95%, preferably 90% or less, the wear resistance shows a favorable result of ②. In addition, when the weight of titanium oxide in the stain-resistant film exceeds 5%, a contact angle is less than 30°, delivering a favorable stain resistance.

[0077]

[Effect of the Invention]

A stain-resistant film is comprised of a photo-resistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function, so as to be resistant to heavy stains, to have a sufficient film strength not to be scratched, and to avoid bacterial growth.

[Brief Description of the Drawings]

Fig. 1

It is a conceptual diagram showing one embodiment of the present invention.

Fig. 2

It is a conceptual diagram showing another embodiment of the present invention.

Fig. 3

It is an Auger electron spectroscopy profile diagram of an intermediate member produced in the producing step of a stain-resistant member according to the present invention; (a) is a sample outermost surface, (b) is at 20 nm under the

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sample outermost surface, and (c) is at 200 nm under the sample outermost surface.

Fig. 4

It is a diagram of an apparatus showing a method of evaluating stain resistance.

Fig. 5

It is a diagram showing the relation between a contact angle with water and stain adhesion.

Fig. 6

It is a diagram showing the relation between the weight of titanium oxide, wear resistance and a contact angle in a stain-resistant film.

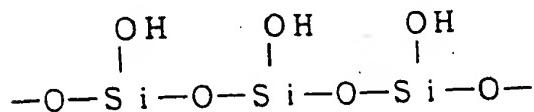
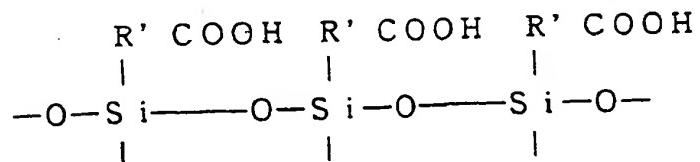
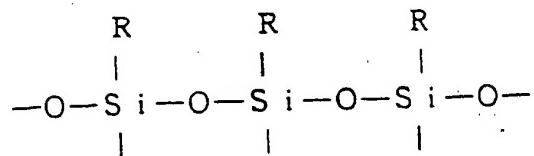
[Explanation of the Reference Numerals]

- 1 Substrate
- 2 Binder layer
- 3 Photo-resistant resin
- 4 Photocatalytic particle
- 5 Metal particle
- 6 Sample
- 7 Artificial bathtub water
- 8 Dirt

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Table 1

Sample	Intermediate member C	Comparing sample A	Intermediate member D	Embodiment sample B
Contact angle (°)	70	70	40	30



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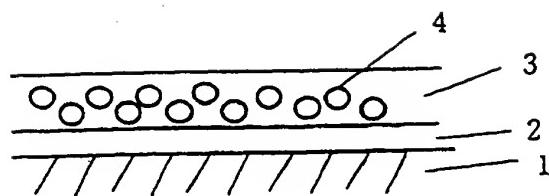


Fig. 1

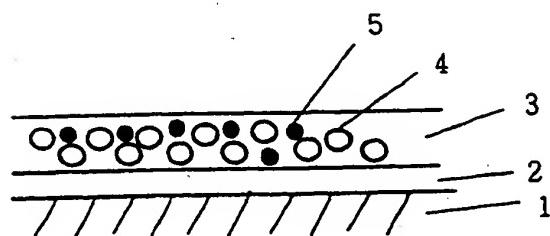


Fig. 2

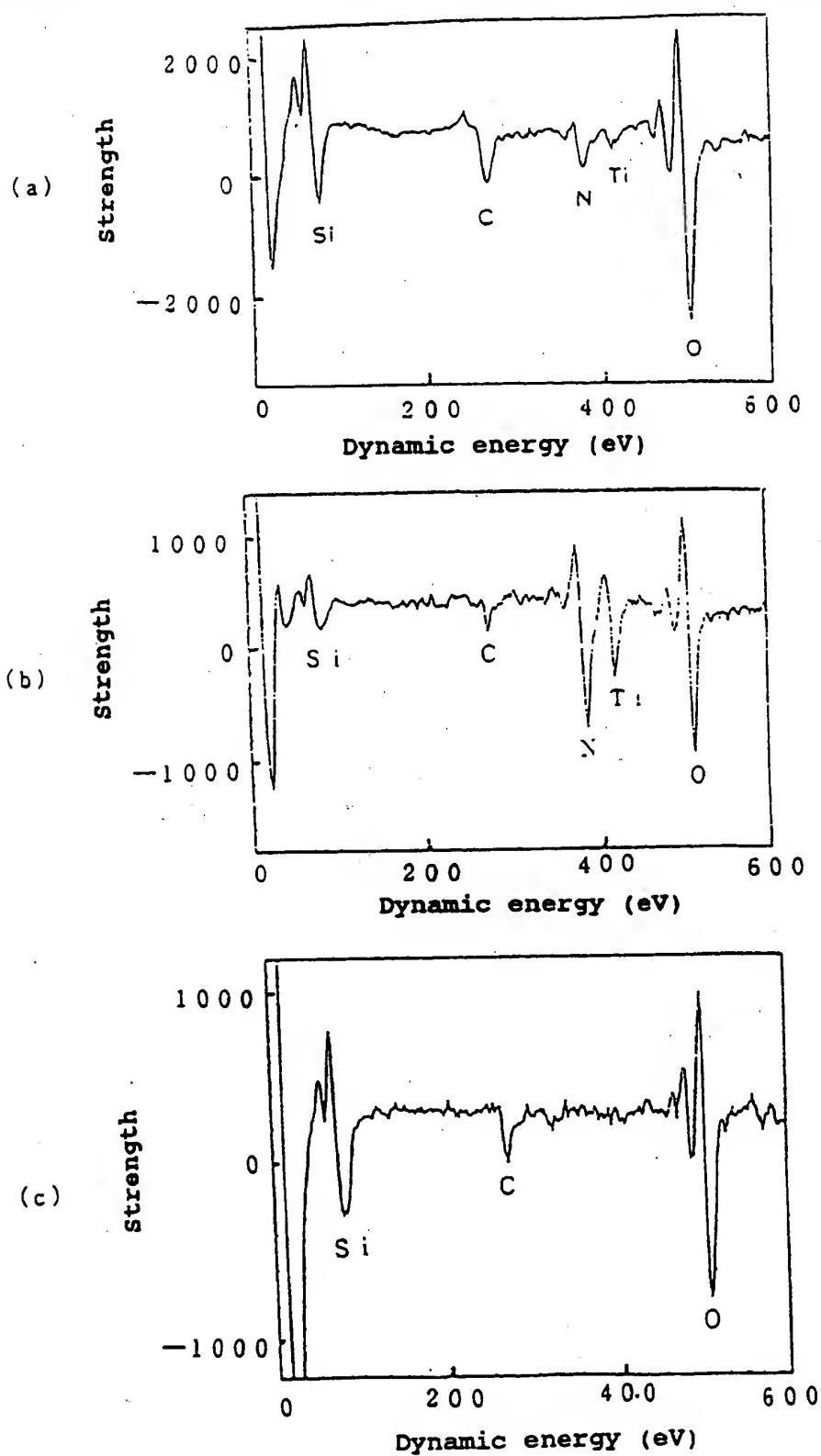


Fig. 3

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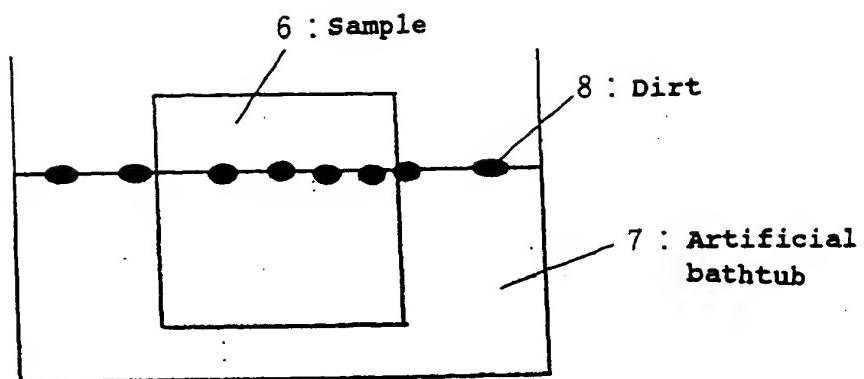


Fig. 4

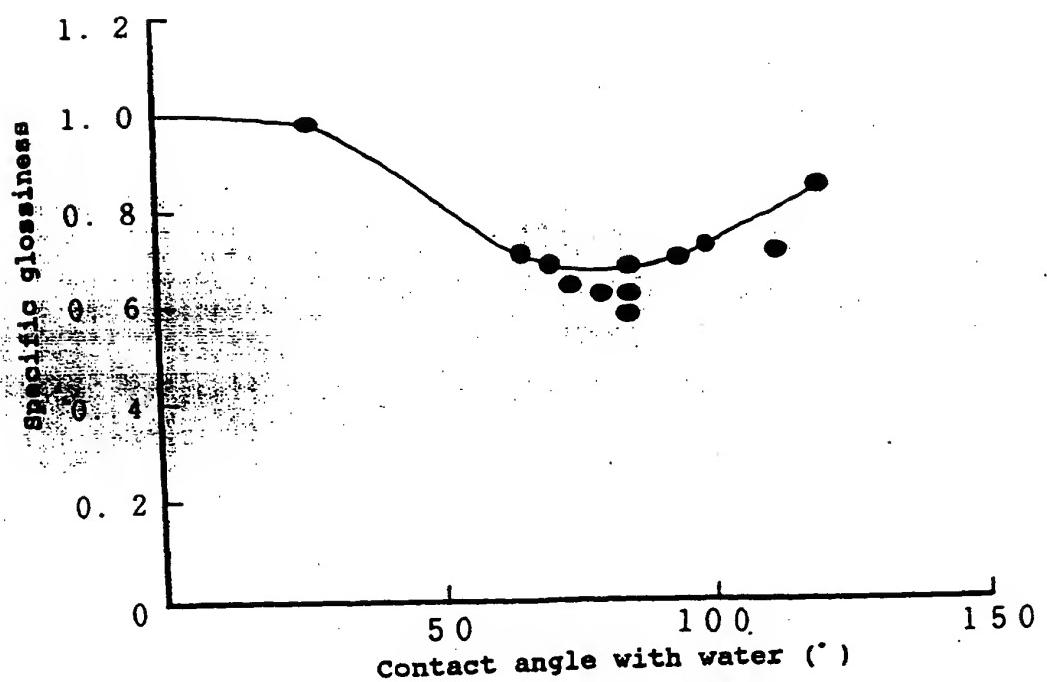


Fig. 5

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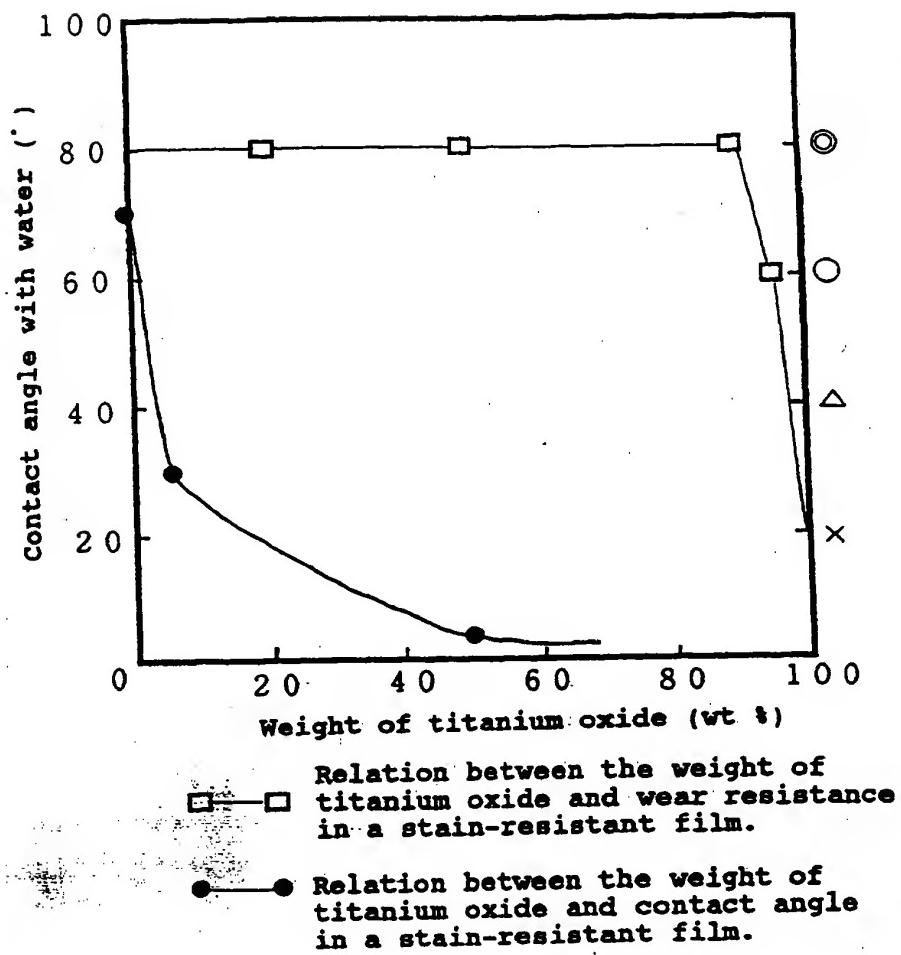


Fig. 6

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ABSTRACT

[Objects]

It is an object of the present invention is to offer a stain-resistant film allowed to be resistant to heavy stains, to have a sufficient film strength not to be scratched, and to avoid bacterial growth.

[Constitution]

A stain-resistant film comprised of a photo-resistant resin whose surface is subjected to a hydrophilization process and a substance having a photocatalytic function.

[Selected Figure]

Fig. 1

30.10.97

D E C L A R A T I O N

In the matter of the
Application for Patent under
EPC in the name of TOTO LTD.

I, the undersigned, Kameichi Nakano, of Kyowa Patent
and Law Office located at 2-3, Marunouchi 3-Chome, Chiyoda-
Ku, Tokyo-To, Japan, do solemnly and sincerely declare as
follows:

1. I am well acquainted with the English and
Japanese languages and am competent to translate from
Japanese into English.

2. I have executed to the best of my ability a true
and correct translation into English of the complete
specification and claim(s) originally filed as Japanese
Patent Application No. 117600/1995 dated April 6, 1995.

Dated this 15th day of October, 1997

Kameichi Nakano
Kameichi Nakano

7-117600

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To: The Commissioner of the Patent Office

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Number of Claim(s): 7

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Atsushi KITAMURA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto CHIKUNI

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Toshiya WATANABE

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto HAYAKAWA

Applicant:

Identification Number: 000010087

Name: TOTO LTD.

Representative: Shigeru Ezoe

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List of Documents filed:

Specification 1

Drawing 1

Abstract 1

(Translation)

7-117600

SPECIFICATION

1. TITLE OF THE INVENTION

[Title of the Invention]

Antifogging transparent member

[Claims]

1. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon.
2. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function thereon.
3. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon.
4. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon, via a layer which prevents diffusion of alkali-modified ingredient in the substrate.

5. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function, via a layer which prevents diffusion of alkali-modified ingredient in a glass substrate.

6. The antifogging transparent material in either of claim 4 and claim 5, wherein the layer which prevents diffusion of alkali-modified ingredient is made of a metal having an electron capturing effect.

7. An antifogging transparent member comprising: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon, via a resin binder layer.

[Detail description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an antifogging transparent member suitable for glass plates of automobiles, trains, airplanes, and the like, mirrors of bathrooms and lavatories, optical equipments, windowpanes of buildings, cathode ray tubes, and the like.

[0002]

[Description of Prior Art]

Glass in as-manufactured state shows good hydrophilicity giving a contact angle with water ranging

from 5 to 20 degrees. If the surface of a substrate is hydrophilic, the surface is sufficiently wetted with water, and no water droplet appears on the surface, which should prevents fogging.

In actual, however, polar ingredients such as lower carboxylic acid gradually adsorb onto the surface with time, and the surface is finally hydrophobicized ("Glass Surface Design", Kindai Henshusha, 1983), so the surface likely induces droplets when it contacts with water, and fogging appears.

[0003]

[Problems to be Solved by the Invention]

When glass plates of automobiles, trains, airplanes, and the like are fogged, safety driving in rain is threatened.

If the mirrors in bathrooms, lavatories, and the like are not fogged, face washing is conveniently done. If the cathode ray tubes of TVs, personal computers, and the like are not fogged, our living style becomes more comfortable such that we can take a bath while watching TV.

In this respect, an object of the present invention is to provide a transparent member that does not induce fogging for a long period.

[0004]

[Means to Solve the Problems]

For solving the above-described problems, the present invention provides an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon.

In addition, the present invention provides an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon.

Furthermore, the present invention provides an antifogging transparent member comprising: a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function.

[0005]

According to a favorable mode of the present invention, an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function or a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function, via a layer which prevents diffusion of alkali-modified ingredient in the substrate.

According to a favorable mode of the present invention, the layer which prevents diffusion of alkali-modified ingredient is made of a metal having an electron capturing effect.

[0006]

According to a favorable mode of the present invention, an antifogging transparent member comprises: a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function

thereon, via a resin binder layer.

[0007]

[Constituent of the Present Invention]

With the configuration of a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function, or a surface layer made of a resin made of photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function, or a surface layer made of a hydrophilicized inorganic material and a hydrophilic material having photocatalytic function thereon, antifogging performance sustains for a long period based on the mechanism described below.

[0008]

Owing to the substrate surface made of a hydrophilic material, the surface is uniformly wetted with water, and no water droplet appears. As a result, no local difference in refractive index occurs over the whole surface area, thus eliminating the appearance of fogging.

In addition, owing to the existence of a material having photocatalytic function on the surface of the substrate, polar ingredients in pollutants as absorbable materials, if existed, are decomposed by the photocatalyst, so the hydrophobicization is effectively prevented, which allows to sustain antifogging performance for long time.

[0009]

It is preferable to fix a layer made of hydrophilic material having photocatalytic functions or a layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function, via a layer which prevents

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diffusion of alkali-modified ingredient in the substrate. The reason of preference is that, for example, when the substrate is glass, the alkali-modified ingredient in the glass substrate is prevented from diffusion during firing step to cover the active centers of the material having photocatalytic function.

[0010]

By forming the layer that prevents diffusion of alkali-modified ingredient using a metal having an electron capturing effect, the photocatalytic function is improved as well as the improvement of prevention of diffusion of alkali-modified ingredient. Thus the surface hydrophobicization is further effectively prevented.

[0011]

By forming a layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function onto the surface of a transparent substrate via a resin binder layer, the material having photocatalytic function is further concentrated near to the uppermost layer, thus further effectively preventing the surface from hydrophobicization. In addition, adhesive strength between the substrate and the layer made of a resin made of a hydrophilicized photo-resistant ingredient and a hydrophilic material having photocatalytic function is increased owing to the presence of the resin binder layer.

[0012]

[Embodiments]

Embodiments of the present invention are described below referring to the drawings.

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Fig. 1 shows a practical mode of the present invention, illustrating a structure of a transparent substrate, and a surface layer made of a resin made of a photo-resistant ingredient having a hydrophilicized surface and a hydrophilic material having photocatalytic function thereon.

Fig. 2 shows other practical mode of the present invention, illustrating a structure of a transparent substrate, and a surface layer made of a hydrophilic material having photocatalytic function thereon.

Fig. 3 shows a further practical mode of the present invention, illustrating a structure of a transparent substrate, and a surface layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function thereon.

Fig. 4 shows still other practical mode of the present invention, illustrating a structure of a transparent substrate, and a hydrophilic material having photocatalytic function thereon via a layer which prevents diffusion of alkali-modified ingredient within the substrate.

Fig. 5 shows still further practical mode of the present invention, illustrating a structure of a transparent substrate, and a layer made of a hydrophilic inorganic material and a hydrophilic material having photocatalytic function via a layer which prevents diffusion of alkali-modified ingredient within the substrate.

Fig. 6 shows yet other practical mode of the present invention, illustrating a structure of a transparent substrate, and a layer made of a resin made of a photo-resistant ingredient, which resin surface is hydrophilicized, and a hydrophilic material having

photocatalytic function thereon via a resin binder layer.

[0013]

The hydrophilic material is a material that shows hydrophilicity to a degree of difficult for contaminants to attach thereto, and that has a contact angle of less than 30 degrees with water. Concrete description of the hydrophilic material is given below.

Fig. 7 shows the relation between the contact angle with water and the likeliness of contamination determined on various kinds of resins.

The contact angle with water was determined by the method described below. A specimen was dipped into an artificial bath water (a warm water prepared by mixing human filth, lard, and soap) for three hours, as illustrated in Fig. 8, and relative gloss at near the water surface level before and after the dipping. The relative gloss was taken as an index of likeliness of contamination. The relative gloss is defined as the gloss after the dipping based on the gloss before dipping, or 1.

As seen in Fig. 7, the relative gloss became to minimum at around 70 degrees of contact angle with water, and contamination likely occurred. With the decrease in the contact angle with water, the relative gloss was improved more than the case of increasing the relative gloss. And the relative gloss reached a plateau in a domain below 30 degrees. Accordingly, the hydrophilicity becomes a degree to difficult to be contaminated if only the contact angle with water is less than 30 degrees.

[0014]

Examples of the transparent substrate are glass,

translucent alumina, and translucent plastics.

[0015]

Applicable hydrophilic inorganic material is basically an inorganic oxide, which includes a crystalline material such as partially stabilized zirconia, titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, di-bismuth trioxide, and tin oxide; and glass material such as glaze and silicone. Inorganic non-oxide is also applicable if only it shows hydrophilicity, for example, silicon nitride and silazane. When, however, in the example of Fig. 1, an inorganic oxide or an inorganic non-oxide, having a property of absorbing ultraviolet light, it is preferable to add a metal having an electron capturing effect to support the material having photocatalytic function. One or more of these inorganic hydrophilic materials may be used at a time.

[0016]

The material having photocatalytic function is a material which emits electrons and forms positive holes under irradiation of light having a specific wave length or less, thus being able to generate active oxygen. Examples of that type of material showing hydrophilicity are titanium oxide, zinc oxide, strontium titanate, tungsten trioxide, ferric oxide, di-bismuth trioxide, and tin oxide. One or more of these materials having photocatalytic function may be used at a time.

[0017]

The material having photocatalytic function is preferably containing a metal having an electron capturing effect. The metal having an electron capturing effect is a

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metal such as Pt, Pd, Au, Ag, Cu, Ni, Co, Fe, Co, and Zn, which has a small ionization tendency and which is likely reduced by itself. One or more of these metals may be used at a time. Presence of a metal having an electron capturing effect induces an effect to suppress the degradation of photocatalytic function, which degradation occurs when alkali metal or alkali earth metal ions exist.

[0018]

The resin made of a photo-resistant ingredient is a resin having favorable photo-resistance. Examples of that type of resin are silicone resin, siloxane, resin, polysilazane resin, and fluororesin.

[0019]

The layer preventing diffusion of alkali-modified ingredient in the glass substrate is a layer which prevents the diffusion of alkali-modified ingredient in the glass substrate to the uppermost layer to contact with a material having photocatalytic function thus to degrade the photocatalytic function.

The alkali-modified ingredient is an alkali metal or an alkali earth metal such as sodium, potassium, calcium, and magnesium.

The material of the layer preventing diffusion of alkali-modified ingredient in the glass substrate is basically arbitrary material if only the material has the above-described function. Examples of that type of material are alumina, silica, calcium fluoride, cerium oxide, lanthanum oxide, zirconium oxide, yttrium oxide, zinc sulfate, tantalum oxide, silicon oxide, tin oxide, germanium, tellurium, lanthanum fluoride, platinum, gold,

silver, copper, zinc, iron, nickel, cobalt, and palladium.

[0020]

When platinum, gold, silver, copper, zinc, iron, nickel, cobalt, or palladium is used in the layer preventing the diffusion of alkali-modified ingredient in the glass substrate, the photocatalytic function is enhanced because these elements have an electron capturing effect. Accordingly, the addition of these elements is preferable because the surface hydrophobicization is further effectively prevented.

When, in the case that the glass substrate is made of a low melting point material such as soda glass, a layer made of high purity silica is used in the layer which prevents the diffusion of alkali-modified ingredient in the glass substrate, the sinking of a material having photocatalytic function into the substrate during the firing stage is reduced, thus making the material having photocatalytic function concentrate to the uppermost surface to improve the photocatalytic function. The use of high purity silica layer is preferable because the surface hydrophobicization is further effectively prevented.

[0021]

The resin binder layer shown in Fig. 6 may be the same kind of resin with that of the surface made of a photo-resistant ingredient, and may not be necessarily the same kind therewith. Therefore, more inexpensive resin may be used for molding. As for the resin binder, both of an inorganic binder such as silicone and an organic binder such as thermosetting resin, photo-setting resin, and thermoplastic resin are applicable.

[0022]

The following is an outline of a method for manufacturing an anti-contaminant member shown in Figs. 1 through 6.

First, the description is given to the case of Fig. 1, wherein the transparent substrate is quartz glass, the resin made of a photo-resistant ingredient having a hydrophilicized surface is a siloxane resin derivative to which the surface hydrophilicization is conducted by the method described later, the hydrophilic material having photocatalytic function is anatase titanium oxide, and the anatase titanium oxide contains copper as a material having an electron capturing effect.

In that case, the manufacturing method of the member basically comprises the steps of: preparing a mixed liquid of anatase titanium oxide sol and a solution containing copper ion; preparing an applying liquid by adding siloxane resin, a diluent, and a curing agent to the mixed liquid; applying the applying liquid onto a quartz glass; firing the quartz glass to obtain an intermediate member; irradiating light containing ultraviolet light to the intermediate member to decompose or oxidize a portion made of alkyl and the like in the siloxane resin layer formed on and exposed to the surface, thus hydrophilicizing the surface of the intermediate member.

[0023]

It is preferable that anatase titanium oxide sol is fully dispersed in the suspension. To do this, the dispersion is done in acidic or alkaline state because the anatase titanium oxide has an isoelectric point at pH 6.5.

Surface active agent or dispersant (deflocculating agent) may be added to improve the dispersability. Generally, water, ethanol, and propanol are often used as the solvent to disperse the anatase titanium oxide sol.

[0024]

The solution containing copper ion is preferably a solution of soluble copper compound such as cupric acetate and cupric sulfate. For the case of metal having an electron capturing effect, other than copper, soluble solution of silver nitrate, silver sulfate, silver lactate, and silver acetate are preferable because of simplicity of mixture treatment. As for the solvent used in a solution containing copper ion, it is preferable to use the same kind of material with anatase titanium oxide sol suspension water, though ethanol, and propanol are applicable.

[0025]

In the step for mixing anatase titanium oxide sol suspension with a solution containing copper ion, pH of the solution containing copper ion is preferably adjusted to almost the same with pH of the anatase titanium oxide sol suspension. The reason is that the change in pH of the anatase titanium oxide sol suspension is smaller, thus the pH of the solution containing copper ion does not significantly degrade the dispersability of the anatase titanium oxide sol in the suspension.

[0026]

After mixing the anatase titanium oxide sol suspension with the solution containing copper ion, a light containing ultraviolet light may be irradiated thereto. Irradiation of light containing ultraviolet light makes copper ion

photoreduce to fix onto the anatase titanium oxide particles, so the photocatalytic function is improved.

The light containing ultraviolet light is a light having sufficient energy for reducing metal ion such as copper ion which has an electron capturing effect.

[0027]

It is preferable to prepare the applying liquid by adding siloxane resin, diluent, and curing agent in this sequent order because of giving least possibility of coagulation.

[0028]

The method for applying the liquid onto the surface of quartz glass is basically arbitrary one. An applicable method for applying the liquid includes spray coating method, roll coating method, and dip coating method.

[0029]

The step for heat treatment in that case may be conducted at a low temperature below 100°C for a long period, or may be conducted at 100°C or above and below the heat resistant temperature of the photo-resistant ingredient (Si-O bond section in siloxane resin, for example) in the resin and below the heat resistant temperature of the substrate (quartz glass) for a short period. Generally, particles made of a material having photocatalytic function have heavier specific gravity than a resin containing photo-resistant ingredient, it is preferable to conduct heat treatment at 100°C or above and below the heat resistant temperature of the photo-resistant ingredient (Si-O bond section in siloxane resin, for example) in the resin and below the heat resistant temperature of the substrate

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(quartz glass) because the particles made of a material having photocatalytic function concentrate to the upper layer section made of a material having photocatalytic function, and because the time for hydrophilicization step is shortened by irradiating light containing ultraviolet light onto the surface of the intermediate member, thus oxidizing or decomposing the section structured by alkyl and the like in the siloxane resin layer which is formed on and exposed to the surface.

[0030]

The step for decomposition or oxidization of R section comprising alkyl and the like in siloxane resin formed to expose on the surface of intermediate member presumably proceeds following the reaction shown below under irradiation of light containing ultraviolet light.

[0031]

[Formula 1]

[0032]

The light containing ultraviolet light means a light which has sufficient energy for actuating electrons from valence electron band to conduction band in a material having photocatalytic function. For the case of anatase titanium oxide, light containing a light of less than 400 nm of wavelength is irradiated.

[0033]

Referring to Fig. 2, an illustration is given in the case that the transparent substrate is quartz glass, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In this case, basically the steps include application

of precursor of anatase titanium oxide such as titanium alkoxide onto quartz glass, followed by firing thus applied glass.

[0034]

The precursor of anatase titanium oxide means a material which changes into anatase titanium oxide after fired. Examples of the precursor of anatase titanium oxide are organic titanate such as titanium alkoxide and inorganic titanate such as titanium sulfate. Use of that type of precursor of anatase titanium oxide is preferable because it is applied uniformly onto substrate.

[0035]

The following description on the step to apply a precursor of anatase titanium oxide onto a quartz glass uses titanium tetraethoxide ($(C_2H_5O)_4Ti$), which is a kind of titanium alkoxide, as the precursor of anatase titanium oxide.

[0036]

First, a coating solution is prepared by adding a diluent and hydrochloric acid to titanium tetraethoxide.

A preferable diluent is alcohol such as ethanol and propanol owing to the easiness of handling. Water should be minimized as far as possible. Existence of plenty of water explosively accelerates the hydrolysis of metallic alkoxide, which causes crack generation.

Addition of hydrochloric acid is given to prevent crack generation in succeeding steps of drying and heat treatment.

[0037]

Next, a coating solution is applied onto the substrate. Flow coating method is simple and preferable for applying

metallic alkoxide. Flow coating is preferably conducted in dry air. The dry air does not mean the one free of water but means less water content than ordinary atmospheric air. If the coating is done in ordinary atmospheric air, hydrolysis is excessively accelerated by the moisture in air so that the control of film thickness becomes difficult. For the case of titanium tetraethoxide, preferable coating weight per single cycle of application is 100 μg or less of titanium oxide per cm^2 from the point of prevention of crack generation.

[0038]

A titanium oxide film is formed after drying the applied substrate in dry air for 1 to 10 min. The principle of obtaining titanium oxide in the above-described steps is the following. First, titanium tetraethoxide as the starting material is hydrolyzed by water in dry air during the flow coating to yield a hydroxide of titanium. Then, dehydration condensation occurs during the drying step to yield amorphous titanium oxide on the substrate. The titanium oxide particles generated have individual particle size of several nanometers and are high purity. Consequently, thus obtained titanium oxide is sintered at a lower temperature than titanium oxide prepared by other methods..

[0039]

When the applied product obtained from the above-described procedure is fired at 400°C or above, the amorphous titanium oxide crystallizes to yield an antifogging transparent member having anatase titanium oxide film which is dense and hydrophilic structure.

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[0040]

Next description is in the case that, in Fig. 3, the transparent substrate is quartz glass, the hydrophilic inorganic material is a low melting point glass ingredient, the hydrophilic material having photocatalytic function is anatase titanium oxide, and the anatase titanium oxide contains copper as a material having an electron capturing effect.

In that case, the basic preparation steps are a sequent order of: a step for preparing a mixed liquid by mixing anatase titanium oxide sol with a solution containing copper ion; a step for preparing an applying liquid by mixing a low melting point glass ingredient to thus prepared mixed solution; a step for applying thus prepared applying liquid onto a quartz glass; and a step for firing the glass.

[0041]

The low melting point glass means a glass composition having lower melting point than the substrate. In this case, the glass composition has lower melting point than that of quartz glass.

[0042]

The following description is for Fig. 4 wherein the transparent substrate is soda glass, the layer to prevent diffusion of alkali-modified ingredient in the substrate is silica glass, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In this case, the basic steps includes: a step for applying a precursor of silica glass such as silicon alkoxide onto a soda glass; a step for applying a alkoxide onto a quartz glass; and a step for firing the glass.

[0043]

The step for applying the precursor of silica glass such as alkoxide onto the soda glass is performed by the following procedure.

First, the coating solution is prepared by adding a diluent, water, and hydrochloric acid to tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$).

The reason of addition of water is that alkoxy silane is stable compared with alkoxide of transient metal such as titanium so that it is hard to induce hydrolysis, thus enhancement of hydrolysis is needed.

Since the prepared coating solution generates heat under water addition, the flow coating onto the substrate is recommended to begin after allowed the coating solution to stand for about 1 hour.

[0044]

The following description is for Fig. 5 wherein the transparent substrate is soda containing translucent alumina, the layer to prevent diffusion of alkali-modified ingredient in the substrate is silica glass, the hydrophilic inorganic material is silica glass, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In this case, the basic steps include: a step for applying silica component such as silicon alkoxide onto the soda-containing translucent alumina; a step for applying a mixture of massive silica such as frit and anatase titanium oxide sol onto the applied silica component; and a step for firing them.

[0045]

The following description is for Fig. 6 wherein the transparent substrate is soda glass, the resin binder layer is siloxane resin, the resin made of a photo-resistant ingredient which surface is hydrophilicized is a siloxane resin derivative which is hydrophilicized on the surface thereof by a method described later, and the hydrophilic material having photocatalytic function is anatase titanium oxide.

In that case, basic procedure for preparation comprises: a step for applying a mixed liquid of siloxane resin and a curing agent onto the soda glass; a step for mixing anatase titanium oxide sol with a solution containing copper ion; a step for adding siloxane resin, a diluent, and a curing agent to the mixed solution to prepare an applying liquid; a step for applying thus prepared applying liquid onto the soda glass; a step for firing the soda glass to obtain an intermediate member; a step for irradiating light containing ultraviolet light to the intermediate member thus inducing decomposition or oxidization of a portion made of alkyl and the like in the siloxane resin layer formed on and exposed to the surface to make the member hydrophilic.

[0046]

The following is effects of the above-described embodiments on the basis of concrete evaluation experiments.

(Evaluation experiment 1)

Tetraethoxysilane, 36% hydrochloric acid, pure water, and ethanol were mixed together at respective weight ratio of 6 : 2 : 6 : 86. The mixture was allowed to stand for 1

hr, then the mixture was applied onto the surface of soda glass by the flow coating method to obtain an intermediate member P.

Titanium tetraethoxide and ethanol were mixed at respective weight ratio of 1 : 9, to which 36% hydrochloric acid was further added at 10 wt.% to the titanium tetraethoxide to obtain a coating liquid. The coating liquid was applied onto the surface of the intermediate member P in dry air by the flow coating method. The coating weight per application was adjusted to 45 ug-titanium oxide per square centimeter.

After then, the applied intermediate member P was dried in dry air for a period of from 1 to 10 min, followed by firing at 500°C to obtain a specimen Q.

The surface of the specimen Q was applied by 1 wt.% copper acetate aqueous solution using the spray coating method. The light of 20W BLB fluorescent lamp was irradiated onto the surface of Q from a distance of 20 cm to obtain a specimen A. Observation of the specimen A proved to have a sufficient translucent property.

The characteristics of antifogging performance, contact angle with water, anti-bacterial performance, anti-odor property, and anti-abrasion property were evaluated for the specimen A, and also for a soda glass and the intermediate member P for comparison.

[0047]

As for the antifogging property, an as-prepared specimen and a specimen after irradiated by BLB fluorescent lamp for 1 month were treated by breathing method to provide fog on the surface thereof, then the presence/absence of

water droplet on the surface was checked under a microscope.

For the contact angle with water, an as-prepared specimen and a specimen after irradiated by BLB fluorescent lamp for 1 month were determined for the angle of contact using a contact angle meter.

The result is shown in Table 1.

[0048]

[Table 1]

[0049]

Since the soda glass substrate has a significantly hydrophobic property giving 50 degrees of contact angle with water, the soda glass after prepared the specimen showed the generation of water droplets. To the contrary, the specimen A and the intermediate member P did not show water droplet on the surface because they have a small contact angle with water, less than about 1 degree, and they are sufficiently hydrophilicized.

After irradiating BLB fluorescent lamp for 1 month, the soda glass substrate and the intermediate member P were hydrophobicized to a significant degree, giving 53 degrees and 49 degrees of contact angle with water, respectively, and generated water droplets. On the specimen A, however, the contact angle with water was 3 degree, which indicated a progress of hydrophilicization, and no water droplet was observed.

[0050]

As for the anti-bacterial property, the evaluation was given using W3110 strain of Escherichia coli.

A glass plate (100 x 100) on which 0.15 ml of bacterial

liquid (10000 - 50000 CFU) was dropwise added was attached to the uppermost surface of each of the above-described specimens which were preliminarily sterilized by 70% ethanol. White light (3500 lux) was irradiated to each of the specimens for 30 min. The bacteria liquid was wiped off using a sterilized gauze, which was then recovered into 10 ml of physiological salt solution. Thus the survival rate was determined to use as the index of evaluation. The criteria of index are listed below.

- +++: Less than 10% of survival rate of Escherichia coli.
- ++: Ten percent or more and less than 30% of survival rate of Escherichia coli.
- +: Thirty percent or more and less than 70% of survival rate of Escherichia coli.
- : Seventy percent or more of survival rate of Escherichia coli.

The evaluation of soda glass substrate and of intermediate member P was (-), and the specimen A showed (++) of good evaluation.

[0051]

The evaluation of odor prevention was determined by measuring R30(L) value. The term R30(L) means the rejection rate of odor ingredient after the irradiation of light. In concrete terms, the steps for determining R30(L) are: placing a specimen in an 11 liter glass container facing the surface covered with antifogging film to the light source (4 w BLB lamp) at a distance of 8 cm; injecting methylmercaptan gas into the container to create 3 ppm of initial concentration; irradiating light against the specimen surface for 30 min; then determining the change in

concentration of the gas.

The value of R_{30(L)} was less than 10% for the soda glass and the intermediate member P, and was 90% or more for the specimen A.

Regarding the anti-abrasion characteristic, a rubbing abrasion was given to the surface of each specimen using a plastics eraser, then the change of appearance was observed. The criterion of the evaluation on the anti-abrasion characteristic is given below.

- ◎ : No change occurred after 40 cycles of traverse.
- : Flaw appeared and the surface layer was separated after traversing cycles of 10 or more and less than 40.
- △ : Flaw appeared and the surface layer was separated after traversing cycles of 5 or more and less than 10.
- × : Flaw appeared and the surface layer was separated after less than 5 cycles of traverse.

Favorable results (◎) were obtained for all of the soda glass substrate, the intermediate member P, and the specimen A.

[0053]

(Evaluation experiment 2)

A solution of siloxane resin containing a curing agent was applied onto a transparent acrylic plastics substrate (10 cm square). The substrate was treated by heat at 140C to prepare an intermediate member S. A liquid was prepared by: mixing a nitric acid suspension of titanium oxide sol having 0.01 μ m of average suspended particle size, 3 wt.% of aqueous solution of copper acetate, and siloxane resin at a weight part equal to that of solid titanium oxide; diluting the mixture with propanol; further adding a curing agent

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to the mixture; applying thus prepared mixture onto the surface of the intermediate member S; then heat-treating the intermediate member S at 140°C to obtain an intermediate member T. A ELB lamp light was irradiated against the intermediate member T for 5 days to obtain a specimen B. For the specimen B and an acrylic plate as a reference material.

For each of the specimen and the intermediate member, evaluation was given on the antifogging property, the contact angle with water, the anti-bacterial property, the odor preventive performance, and the anti-abrasion property. The method of evaluation was the same with that used in Evaluation experiment 1.

[0054]

For the acrylic plate, the contact angle with water showed 70 degrees for both before and after 1 month of BLB fluorescent lamp light irradiation, which suggested that the plate was hydrophobicized to significant degree. In fact, the acrylic plate showed generation of water droplets. To the contrary, the specimen B showed a small contact angle with water, or 3 to 9 degrees. The specimen was sufficiently hydrophilicized on its surface, and no water droplet was observed on the surface.

For the anti-bacterial property, the acrylic plate gave the result of (-), and the specimen B provided a good result of (+++).

As for the anti-odor property, the acrylic plate gave the value of less than 10%, and the specimen B provided a good result giving more than 90%.

Regarding the anti-abrasion property, both the acrylic

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plate and the specimen B showed favorable result of oo mark.

[0055]

[Effect of the Invention]

Favorable anti-fogging performance is sustained for a long period by covering the transparent substrate with: a layer made of a hydrophilic material having photocatalytic function thereon; or a layer made of a resin made of a photo-resistant ingredient hydrophilicized at the surface thereof and a hydrophilic material having photocatalytic function; or a layer made of an inorganic material having hydrophilic material and a hydrophilic material having photocatalytic function.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 shows an example of the present invention.

[Fig. 2]

Fig. 2 shows other example of the present invention.

[Fig. 3]

Fig. 3 shows further example of the present invention.

[Fig. 4]

Fig. 4 shows still other example of the present invention.

[Fig. 5]

Fig. 5 shows still further example of the present invention.

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[Fig. 6]

Fig. 6 shows yet other example of the present invention.

[Fig. 7]

Fig. 7 shows the relation between the contact angle with water and the likeliness of contaminant adhesion.

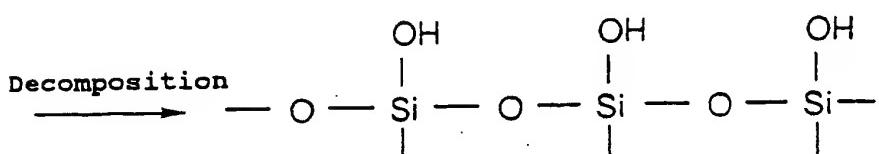
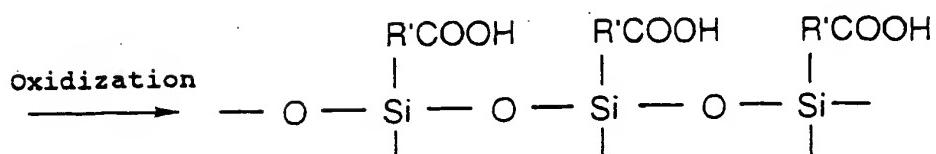
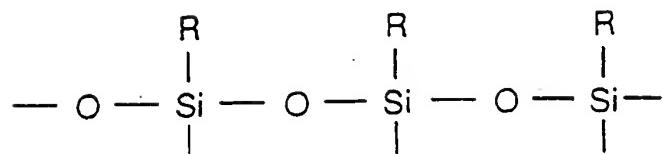
[Fig. 8]

Fig. 8 illustrates an evaluation device for anti-contamination property.

[Description of the Reference Symbols]

- 1: transparent substrate
- 2: resin made of a photo-resistant ingredient, which surface is hydrophilicized
- 3: hydrophilic material having photocatalytic function
- 4: inorganic material having hydrophilic property
- 5: layer to prevent diffusion of alkali modified ingredient in substrate
- 6: resin binder layer
- 7: filth
- 8: artificial bath water
- 9: specimen

[Formula 1]



[Table 1]

	After preparing specimen		After 1 month has passed	
	Contact angle to water (°)	Antifogging property	Contact angle to water (°)	Antifogging property
Specimen A	10	Absence of water droplet	3	Absence of water droplet
Soda glass	50	Absence of water droplet	53	Absence of water droplet
Intermediate member P	9	Absence of water droplet	49	Absence of water droplet

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Fig. 1

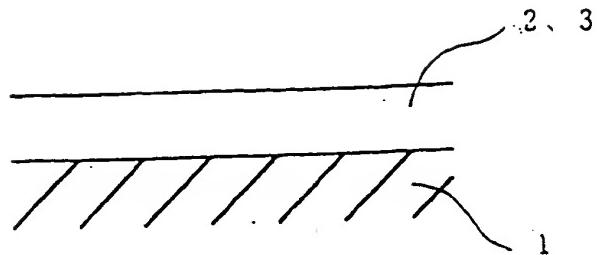


Fig. 2

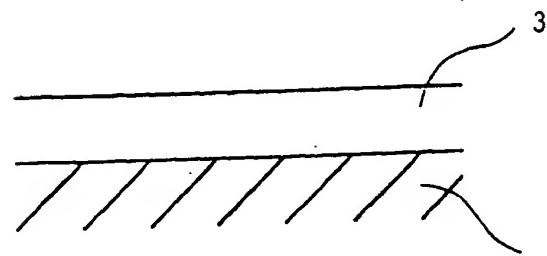


Fig. 3

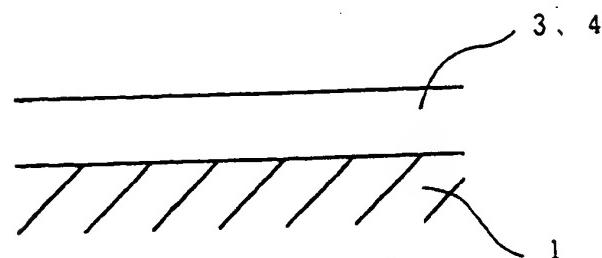
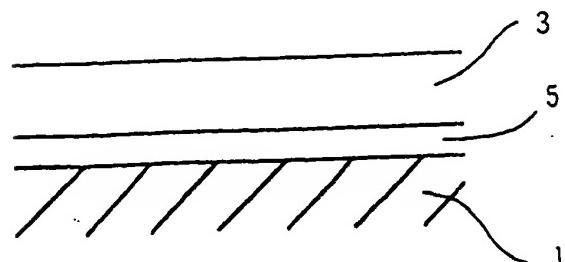


Fig. 4



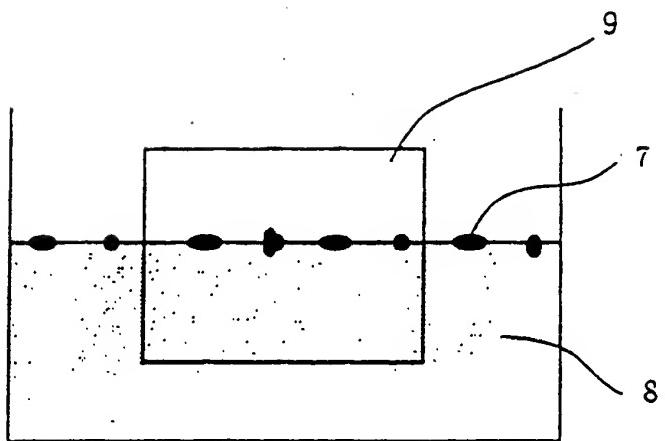
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Fig. 8



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Fig. 5

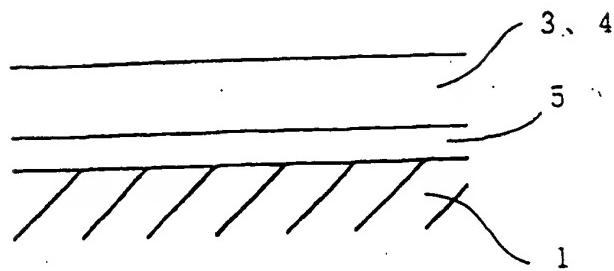


Fig. 6

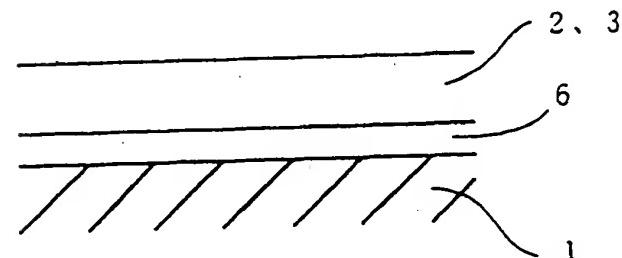
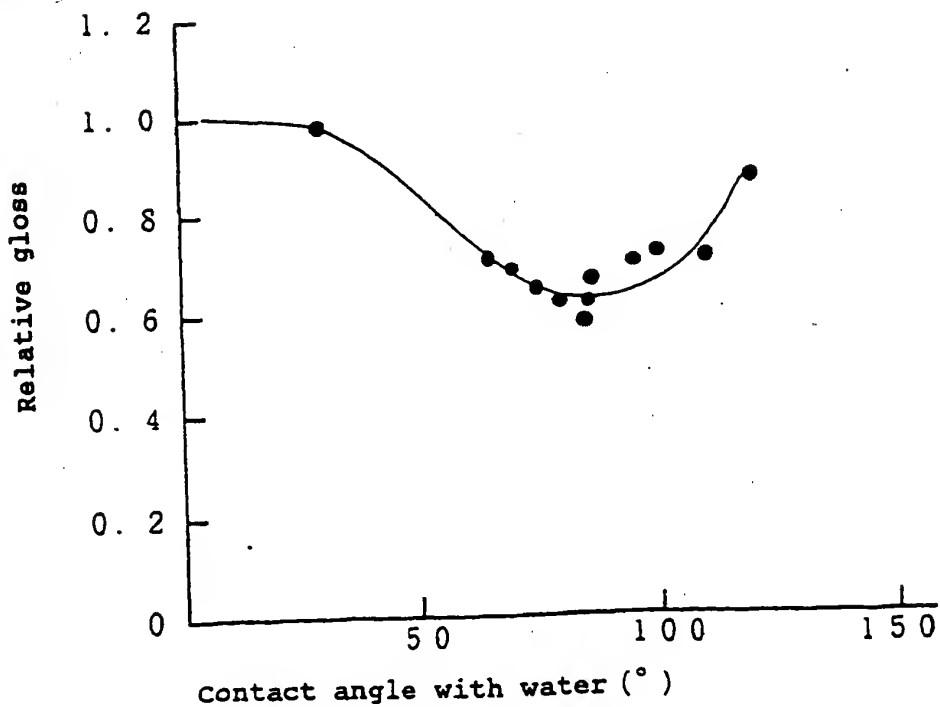


Fig. 7



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ABSTRACT

[Object]

To provide an antifogging transparent member sustaining favorable antifogging property for a long period.

[Constituent]

An antifogging member comprises a transparent substrate (1), and a surface layer made of a hydrophilic material (3) having photocatalytic function thereon; or comprises a transparent substrate, and a surface layer made of a resin (2) made of a photo-resistant ingredient hydrophilicized at the surface thereof and a hydrophilic material having photocatalytic function; or comprises a transparent substrate, and a surface layer made of an inorganic material having hydrophilic material and a hydrophilic material having photocatalytic function.

[Selected Drawing]

Fig. 1

D E C L A R A T I O N

In the matter of the
Application for Patent under
EPC in the name of TOTO LTD.

I, the undersigned, Kameichi Nakano, of Kyowa Patent and Law Office located at 2-3, Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, do solemnly and sincerely declare as follows:

1. I am well acquainted with the English and Japanese languages and am competent to translate from Japanese into English.
2. I have executed to the best of my ability a true and correct translation into English of the complete specification and claim(s) originally filed as Japanese Patent Application No. 182020/1995 dated June 14, 1995.

Dated this 15th day of October, 1997

Kameichi Nakano
Kameichi Nakano

7-182020

Name of Document: Patent Application

Reference Number: 955349

Application Date: June 14, 1995

To: The Commissioner of the Patent Office

International Patent Classification: B06B7/12

Title of the Invention: ANTIFOGGING MEMBER, METHOD FOR
PRODUCING THEREOF, AND METHOD FOR
PREVENTING FOGGING OF MEMBER

Number of Claim(s): 104

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto HAYAKAWA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Atsushi KITAMURA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto CHIKUNI

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Toshiya WATANABE

Applicant:

Identification Number: 000010087

Postal code: 802
Address: 1-1, Nakashima 2-Chome, Kokura-Kita-Ku,
Kitakyushu-Shi, Fukuoka-KenName: TOTO LTD.
Representative: Shigeru Ezoe

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Specification 1

Drawing 1

Abstract 1

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SPECIFICATION

1. TITLE OF THE INVENTION

Antifogging member, method for producing thereof, and method for preventing fogging of member

2. Claims

1. Antifogging member comprising a hydrophilic exposed surface and a means for sustaining the hydrophilic exposed surface.

2. The antifogging member of claim 1, comprising a substrate which forms a surface layer thereon having a hydrophilic exposed surface and a means for sustaining the hydrophilic exposed surface.

3. The antifogging member of either claim 1 or claim 2, wherein the means for sustaining the hydrophilic exposed surface is a photocatalyst.

4. The antifogging member of either claim 2 or claim 3, wherein a size of particles and void existing in the surface-layer is 0.2 microns or less.

5. An antifogging member comprising a film made of a hydrophilic material containing a photocatalyst.

6. An antifogging member comprising a substrate and a surface layer made of a hydrophilic catalyst formed thereon.

7. An antifogging member comprising a substrate and a surface layer made of a hydrophilic photocatalyst and of a non-photocatalytic hydrophilic material formed thereon.

8. Antifogging member comprising a substrate and a surface layer made of a hydrophilic photocatalyst and of a non-photocatalytic hydrophilic material formed thereon, while an exposed surface is made of a non-photocatalytic hydrophilic material.

9. The antifogging member of either one of claims 6, 7, and 8, wherein an intermediate layer is sandwiched between the substrate and the surface layer.

10. The antifogging member of either one of claims 7, 8, and 9, wherein the non-photocatalytic hydrophilic material is a hydrophilicized photo-resistant resin.

11. The antifogging member of either one of claims 7, 8, and 9, wherein the non-photocatalytic hydrophilic material is an inorganic amorphous material.

12. The antifogging member of claim 10, wherein the hydrophilicized photo-resistant resin is a resin having Si-O bond or Si-N bond in backbone thereof.

13. The antifogging member of either claims 10 or claim 12, wherein the hydrophilicization is characterized by decomposition or oxidization of a portion of alkyl group or the like included in the resin comprising photo-resistant

ingredient at least at the backbone thereof, which group reacts under irradiation of ultraviolet light.

14. The antifogging member of either one of claims 2, 3, 4, and 6 through 13, wherein the surface layer contains an electron-acquiring metal.

15. The antifogging member of either one of claims 2, 3, 4, and 6 through 13, wherein the surface layer contains an anti-bacterial metal.

16. The antifogging member of either one of claims 2, 3, 4 and 6 through 13, wherein the surface layer contain silver.

17. The antifogging member of claim 5, wherein the film contains an electron-acquiring metal.

18. The antifogging member of claim 5, wherein the film contains an anti-bacterial metal.

19. The antifogging member of claim 5, wherein the film contains silver.

20. The antifogging member of claim 9, wherein the substrate is a glass or a mirror containing an alkali-modified ingredient, and wherein the intermediate layer is a layer to prevent diffusion of the alkali-modified ingredient.

21. The antifogging member of claim 20, wherein the layer to prevent diffusion of the alkali-modified ingredient is a high purity silica layer.

22. The antifogging member of claim 20, wherein the layer to prevent diffusion of the alkali-modified ingredient is a layer containing an electron-acquiring metal.

22. The antifogging member of claim 9, wherein the surface layer comprises a hydrophilicized photo-resistant resin and a photocatalyst, and wherein the intermediate layer is a basecoat layer made of a resin.

24. The antifogging member of claim 5, wherein the film made of a hydrophilic material is a hydrophilicized photo-resistant resin.

25. The antifogging member of either claims 2, 3, 4, and 6 through 16, wherein a part of heat-generating means is added to the surface layer.

26. The antifogging member of either one of claims 5, 17, 18, 19, and 24, wherein a part of the heat-generating means is added to the film.

27. The antifogging member of either one of claims 2, 3, 4, 25, and 26, wherein a part of the heat-generating means is a tin oxide transparent electrode to which a means for impressing voltage is connected.

28. An antifogging member comprising plurality of materials laminated to each other, wherein the surface layer forming the uppermost surface of the laminated materials has a hydrophilic exposed surface and a means for sustaining the hydrophilicity, and wherein a gap is formed between at least a pair of the laminated materials.
29. An antifogging member comprising plurality of materials laminated to each other, wherein the surface layer forming the uppermost surface of the laminated materials has a hydrophilic exposed surface, a means for sustaining the hydrophilicity, and a part of heat-generating means, and wherein a gap is formed between at least a pair of the laminated materials.
30. An antifogging member comprising plurality of materials laminated to each other, wherein the surface layer forming the uppermost surface of the laminated materials has a hydrophilic exposed surface, a tin oxide transparent electrode, and wherein a gap is formed between at least a pair of the laminated materials, and wherein the electrode is connected with a means for impressing voltage thereto.
31. A member comprising a means for irradiating ultraviolet light located at periphery of the member claimed in either one of claims 1 through 30.
32. The member of claim 31, wherein a rim section is located to enclose the means for irradiating ultraviolet light.

33. A member comprising plurality of materials laminated to each other, wherein the surface layer forming the uppermost surface of the laminated materials has a hydrophilic exposed surface and a means for sustaining the hydrophilicity, and wherein a means for irradiating ultraviolet light is sandwiched between at least a pair of the laminated materials.

34. A member comprising a means for irradiating ultraviolet light against rear face of the member claimed in either one of claims 1 through 30.

35. The member of either one of claims 1 through 34, wherein the member is a mirror.

36. The member of either one of claims 1 through 34, wherein the member is a mirror in bathroom or in lavatory.

37. A method for manufacturing antifogging member comprising a hydrophilic film containing a photocatalyst, which method comprising the steps of: preparing a liquid by mixing a photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure the liquid by pouring thereof into a mold; separating thus formed shape from the mold; then irradiating light containing ultraviolet light to the shape.

38. A method for manufacturing antifogging member comprising a hydrophilic film containing a photocatalyst and an anti-bacterial metal, which method comprising the steps

of: mixing a photocatalyst sol with a solution containing an antibacterial metal ion; preparing a liquid by mixing the solution of photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure to liquid by pouring thereof into a mold; separating thus formed shape from the mold; then irradiating light containing ultraviolet light to the shape.

39. A method for manufacturing antifogging member comprising a hydrophilic film containing a photocatalyst and an anti-bacterial metal, which method comprising the steps of: mixing a photocatalyst sol with a solution containing an antibacterial metal ion; irradiating light containing ultraviolet light to the photocatalyst sol solution; preparing a liquid by mixing the solution of irradiated photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure the liquid by pouring thereof into a mold; separating thus formed shape from the mold; then irradiating light containing ultraviolet light to the shape.

40. A method for manufacturing antifogging member comprising a hydrophilic film containing a photocatalyst and an anti-bacterial metal, which method comprising the steps of: preparing a liquid by mixing a photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure the liquid by pouring thereof into a mold; separating thus formed shape from the mold; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light

containing ultraviolet light to the shape.

41. A method for manufacturing antifogging member comprising a hydrophilic film containing a photocatalyst, which method comprising the steps of; applying photocatalytic particles onto the surface of an injection molding die; conducting injection molding within the injection molding die using a compound of thermoplastic resin having a photo-resistant ingredient in backbone thereof; then irradiating light containing ultraviolet light to thus molded shape.

42. A method for manufacturing antifogging member comprising a hydrophilic film containing a photocatalyst, which method comprising the steps of: preparing mixed particles by fixing an anti-bacterial metal to photocatalytic particles; applying the mixed particles onto the surface of an injection molding die; conducting injection molding within the injection molding die using a compound of thermoplastic resin having a photo-resistant ingredient in backbone thereof; then irradiating light containing ultraviolet light to thus molded shape.

43. A method for manufacturing antifogging member comprising a glass substrate and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps of: applying a precursor of photocatalyst onto the surface of the glass substrate; then firing the applied glass substrate.

44. A method for manufacturing antifogging member comprising a glass substrate containing an alkali metal or an alkali earth metal, and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto a glass substrate containing an alkali metal or an alkali earth metal; applying a precursor of photocatalyst onto the surface of the glass substrate; then firing the applied glass substrate.

45. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps of: applying a precursor or photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; then applying silver onto rear face of the glass using the silver mirror reaction.

46. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror, firing the applied glass; applying silver onto rear face of the glass using the silver mirror reaction; then protecting thus formed silver mirror section using a resin composition and the like.

47. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps

of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; then applying silver onto rear face of the glass using the silver mirror reaction.

48. A method of manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto a glass substrate before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; applying silver onto rear face of the glass using the silver mirror reaction; then protecting thus formed silver mirror section using a resin composition and the like.

49. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps of: after fabricating the mirror, applying a precursor of photocatalyst onto the surface of the mirror; then firing the applied mirror.

50. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprising the steps of: after fabricating the mirror, forming a glass layer containing no alkali metal nor alkali earth metal onto the

surface of the mirror; applying a precursor of photocatalyst onto the glass layer; then firing the applied mirror.

51. A method for manufacturing antifogging member comprising a glass substrate, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: applying a precursor of photocatalyst onto the surface of the glass substrate; firing the applied glass substrate; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; then irradiating light including ultraviolet light to the shape.

52. A method for manufacturing antifogging member comprising a glass substrate, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of the glass substrate; applying a precursor of photocatalyst onto the glass substrate; firing the applied glass layer; applying solution containing an anti-bacterial metal ion onto the surface of the layer of applied precursor of photocatalyst; then irradiating light including ultraviolet light to thus fired shape.

53. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating

the mirror; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of the fired shape; irradiating light including ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

54. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; irradiating light including ultraviolet light to the shape; fixing silver onto rear face of the shape using the silver mirror reaction; then protecting thus formed silver mirror section with a resin composition or the like.

55. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; fixing silver onto rear face of thus fired shape using the silver mirror reaction; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light including ultraviolet light to the shape.

56. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and anti-bacterial metal, which method comprising the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; fixing silver onto rear face of thus fired shape using the silver mirror reaction; protecting thus formed silver mirror section with a resin composition or the like; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light including ultraviolet light to the shape.

57. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: after fabricating the mirror, applying a precursor of photocatalyst onto the surface of the mirror; firing the applied mirror; applying a solution containing an anti-bacterial metal ion onto the surface of the fired mirror; then irradiating light including ultraviolet light to the mirror.

58. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass

layer; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; irradiating light including ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

59. A method for manufacturing antifogging member comprising a mirror, at a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; irradiating light including ultraviolet light to the shape; fixing silver onto rear face of the shape using the silver mirror reaction; then protecting thus formed silver mirror section using a resin composition or the like.

60. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; fixing silver onto rear face of thus fired shape using the silver mirror reaction;

applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light including ultraviolet light to the shape.

61. A method for manufacturing antifogging member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; fixing silver onto the rear face of thus fired shape using the silver mirror reaction; protecting thus formed silver mirror section using a resin composition or the like; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light including ultraviolet light to the shape.

62. A method for manufacturing antifogging-member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprising the steps of: after fabricating the mirror, forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; then irradiating light including ultraviolet light to the shape.

63. The method for manufacturing antifogging member of

either one of claims 43 through 62, wherein the step for applying precursor of photocatalyst onto the surface of a substrate comprises the steps of: preparing an applying liquid by adding a diluent and a hydrolysis suppressor to alkoxide which is a precursor of photocatalyst; then applying the prepared liquid onto the surface of the glass substrate.

64. The method for manufacturing antifogging member of either one of claims 44, 47, 48, 50, 52, and 58 through 62, wherein the step for forming a glass layer containing no alkali metal nor alkali earth metal is a step for applying a precursor of silicon glass onto the surface of a glass substrate.

65. The method for manufacturing antifogging member of either one of claims 44, 47, 48, 50, 52, and 58 through 62, wherein the step for forming a glass layer containing no alkali metal nor alkali earth metal comprises the steps of: preparing an applying liquid by adding a diluent, water, and a hydrolysis suppressor to alkoxide which is a precursor of silicon glass; then applying thus prepared liquid onto the surface of a glass substrate.

66. The method for manufacturing antifogging member of claim 63, wherein the step for applying the applying liquid onto the surface of a substrate is conducted using dry air.

67. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a

hydrophilic photocatalyst and a hydrophilic material, which method comprising the steps of: preparing a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin; applying thus prepared liquid onto the surface of the substrate; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

68. A method for manufacturing antifogging member comprising a substrate, and surface layer made of a hydrophilic photocatalyst and a hydrophilic material, which method comprising the steps of: forming a basecoat layer onto the surface of the substrate; applying a liquid containing a photocatalyst and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

69. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: mixing a photocatalyst sol and a solution containing an anti-bacterial metal ion; preparing a liquid by adding a photo-resistant thermosetting resin to the solution; applying the liquid onto the basecoat layer; heating to cure the applied liquid; then irradiating light containing ultraviolet light to the cured shape.

70. A method for manufacturing antifogging member

comprising a substrate, and a surface layer made of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: forming a basecoat layer onto the surface of the substrate; mixing a photocatalyst sol and a solution containing an anti-bacterial metal ion; preparing a liquid by adding a photo-resistant thermosetting resin to the solution; applying the liquid onto the surface of the substrate; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

71. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: preparing a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin; applying the liquid onto the surface of the substrate; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

72. A method for manufacturing antifogging mamber comprising a substrate, and a surface layer made of a hydrophilic photocatalyst and hydrophilic material, which method comprising the steps of: forming a basecoat layer onto the surface of the substrate; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of the basecoat layer; heating to cure the applied liquid; applying a solution

containing an anti-bacterial metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

73. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a hydrophilic photocatalyst and a hydrophilic material, which method comprising the steps of: after fabricating a mirror, applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of the mirror; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

74. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprising the steps of: after fabricating a mirror, forming a basecoat layer onto the surface of the mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

75. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprising the steps of: applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror; heating to cure the applied liquid; irradiating

light containing ultraviolet light to thus cured shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

76. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprising the steps of: forming a basecoat layer onto the surface of glass before fabricating a mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; irradiating light containing ultraviolet light to thus cured shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

77. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprising the steps of: applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror; heating to cure the applied liquid; fixing silver onto rear face of thus cured shape using the silver mirror reaction; then irradiating light containing ultraviolet light to the shape.

78. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which

method comprising the steps of: forming a basecoat layer onto the surface of a glass before fabricating a mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; fixing silver onto rear face of thus cured shape using the silver mirror reaction; then irradiating light containing ultraviolet light to the shape.

79. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: after fabricating a mirror, mixing a photocatalyst sol with a solution containing anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixed solution; applying thus prepared solution onto the surface of the mirror; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

80. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: after fabricating a mirror, forming a basecoat layer on the surface of the mirror; mixing a photocatalyst sol with a solution containing anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixed solution; applying thus prepared liquid onto the basecoat layer; heating to cure the applied liquid; then irradiating light

containing ultraviolet light to thus cured shape.

81. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: after fabricating a mirror, applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of the mirror; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

82. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: after fabricating a mirror, forming a basecoat layer on the mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure to applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

83. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: mixing a photocatalyst sol with a solution containing an

anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixture; applying thus prepared solution onto the surface of a glass before fabricating a mirror; heating to cure the applied solution; irradiating light containing ultraviolet light to the cured shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

84. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: forming a basecoat layer on the surface of a glass before fabricating a mirror; mixing a photocatalyst sol with a solution containing an anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixture; applying thus prepared solution onto the surface of the basecoat layer; heating to cure the applied solution; irradiating light containing ultraviolet light to thus cured shape; then fixing silver onto the rear face of the shape using the silver mirror reaction.

85. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror; heating to cure the applied liquid; applying a solution containing an

anti-bacterial metal ion onto thus cured shape; irradiating light containing ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

86. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: forming a basecoat layer onto the surface of a glass before fabricating a mirror; applying liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal iron onto thus cured shape; irradiating light containing ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

87. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror; heating to cure the applied liquid; fixing silver onto rear face of thus cured shape using the silver mirror reaction; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light containing ultraviolet light to the shape.

88. A method for manufacturing antifogging member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprising the steps of: forming a basecoat layer onto the surface of a glass before fabricating a mirror; applying a liquid containing a photocatalyst sol and photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; fixing silver onto rear face of thus cured shape using the silver mirror reaction; applying a solution containing an anti-bacterial metal ion onto the shape; then irradiating light containing ultraviolet light to the shape.

89. The method for manufacturing antifogging member of either one of claims 68, 70, 72, 74, 78, 80, 82, 84, 86, and 88, wherein a drying step is inserted after completing the step for forming the basecoat layer.

90. A method for manufacturing antifogging member comprising: attaching a film described in claims 5, 17, 18, 19, 24, and 26, to the substrate.

91. A method for manufacturing antifogging member comprising: attaching the film described in claims 5, 17, 18, 19, 24, and 26, to the substrate via a binder.

92. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material, while exposed surface being consisted only of the hydrophilic material,

which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; then firing the shape again.

93. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; applying an amorphous material onto the applied photocatalyst sol; then firing the applied substrate.

94. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a mixed solution of a photocatalyst sol and an anti-bacterial metal ion onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; then firing again the applied substrate.

95. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of:

applying a mixture of a photocatalyst sol and a solution containing an anti-bacterial metal ion onto the surface of the substrate; applying an amorphous material onto the applied mixed solution; then firing the applied substrate.

96. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; firing the applied shape again; applying a solution containing an anti-bacterial metal ion onto thus re-fired shape; then irradiating light containing ultraviolet light to the shape.

97. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; applying an amorphous material onto the photocatalyst sol layer; firing the applied substrate; applying a solution containing an anti-bacterial metal ion onto thus re-fired shape; then irradiating light containing ultraviolet light to the shape.

98. A method for manufacturing antifogging member

comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; applying a solution containing an anti-bacterial metal ion onto the applied amorphous material; then firing the substrate again.

99. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; applying an amorphous material onto the applied sol layer; applying a solution containing an anti-bacterial metallic ion onto the applied amorphous material; then firing the substrate.

100. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; applying a solution containing an anti-bacterial metallic ion onto the applied photocatalyst sol layer; applying an amorphous material onto the applied anti-

bacterial metallic ion layer; then firing the substrate.

101. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying a solution containing an anti-bacterial metallic ion onto thus fired shape; applying an amorphous material onto the applied anti-bacterial metallic ion layer; then firing the substrate again.

102. A method for manufacturing antifogging member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprising the steps of: applying a photocatalyst sol onto the surface of the substrate; applying a solution containing an anti-bacterial metallic ion onto the applied photocatalyst sol layer; firing the applied substrate; applying an amorphous material onto thus fired shape; then firing the substrate again.

103. A method for preventing fogging of a member comprising: supplying dry air against the surface of the member having a hydrophilic exposed surface and having a means to sustain hydrophilicity.

104. A method for preventing fogging of a member comprising: irradiating ultraviolet light against the surface of the member having a hydrophilic exposed surface and having a means to sustain hydrophilicity.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a member provided by antifogging function and a method for manufacturing the member, which member is glass plates of automobiles, trains, airplanes, and the like, mirrors of bathrooms and lavatories, optical equipments, windowpanes of buildings, cathode ray tubes, and the like, and which member functions by letting light penetrate or reflect, (which member is hereinafter referred to simply as "translucent member"), and relates to an antifogging art for the translucent member.

[0002]

[Description of the Prior Art]

When glass plates of automobiles, trains, airplanes, and the like are fogged, safety driving thereof in rain is threatened.

If the mirrors in bathrooms, lavatories, and the like are not fogged, face washing is conveniently done. If the cathode ray tubes of TVs, personal computers, and the like are not fogged, our living style becomes more comfortable such that we can take a bath while watching TV.

[0003]

The mechanism of fogging on the surface of a member is the following. When water vapor molecules generated exceed

their saturation vapor pressure within an enclosed space, the water vapor molecules higher than the saturation vapor pressure are rejected from the vapor system. That is, the excess amount of water vapor molecules attach to solid materials in the enclosed space, to wall surface and floor surface, thus developing water droplets.

[0004]

To this point, the conventional antifogging art against these translucent members is to avoid the generation of saturation vapor pressure in the vicinity of the members.

In concrete terms, a transparent material layer which generates heat under application of electricity is formed on the surface of target member, thus increasing the surface temperature of the member. Alternatively, the surface of the target member is kept at or below the saturation pressure by charging dry air against the member surface.

[0005]

[Problems to be Solved by the Invention]

With the method to increase the surface temperature of the target member by forming a transparent material layer which generates heat by applying electricity onto the surface of the material, however, the desired surface temperature on the member surface cannot be sustained unless the electricity is applied continuously. The method is uneconomical one for antifogging art for a long period. Furthermore, the method is difficult to completely eliminate once occurred fog from the member surface.

The method to keep the surface of target member at or below the saturation vapor pressure by charging dry air against the surface of the member is also an uneconomical

method particularly in bathrooms because the method needs to continuously charge dry air. In addition, the method is also difficult to completely eliminate once occurred fog from the member surface.

The present invention was derived to cope with the situation, and an object of the present invention is to provide a translucent member that sustains antifogging effect for a long period.

[0006]

[Means to Solve the Problems]

To solve the above-described problems, the present invention provides an antifogging translucent member comprising a hydrophilic exposed surface and a means for sustaining the hydrophilic exposed surface.

[0007]

According to a preferred mode of the present invention, the antifogging member comprises a substrate, and a surface layer having a hydrophilic exposed surface having a means for sustaining the hydrophilic exposed surface.

[0008]

According to a preferred mode of the present invention, the means for sustaining the hydrophilic exposed surface is a photocatalyst.

[0009]

According to a preferred mode of the present invention, the size of particles and voids existing in the surface layer is 0.2 microns or less.

[0010]

According to a preferred mode of the present invention, a film made of a hydrophilic material contains a

photocatalyst.

[0011]

According to a preferred mode of the present invention, a surface layer consisting of a hydrophilic catalyst is formed on the substrate.

[0012]

According to a preferred mode of the present invention, a surface layer consisting of a hydrophilic photocatalyst and of a non-photocatalytic hydrophilic material is formed on the substrate.

[0013]

According to a preferred mode of the present invention, a surface layer consisting of a hydrophilic photocatalyst and of a non-photocatalytic hydrophilic material is formed on the substrate, while an exposed surface is made of a non-photocatalytic hydrophilic material.

[0014]

According to a preferred mode of the present invention, an intermediate layer is sandwiched between the substrate and the surface layer.

[0015]

According to a preferred mode of the present invention, the non-photocatalytic hydrophilic material is a hydrophilicized photo-resistant resin.

[0016]

According to a preferred mode of the present invention, the non-photocatalytic hydrophilic material is an inorganic amorphous material.

[0017]

According to a preferred mode of the present invention,

the hydrophilicized photo-resistant resin is a resin having Si-O bond or Si-N bond in backbone thereof.

[0018]

According to a preferred mode of the present invention, the hydrophilicization is characterized by decomposition or oxidization of a portion of alkyl group or the like included in the resin comprising photo-resistant ingredient at least at the backbone thereof, which group reacts under irradiation of ultraviolet light.

[0019]

According to a preferred mode of the present invention, the surface layer contains an electron-acquiring metal.

[0020]

According to a preferred mode of the present invention, the surface layer contains an anti-bacterial metal.

[0021]

According to a preferred mode of the present invention, the surface layer contains silver.

[0022]

According to a preferred mode of the present invention, the film contains an electron-acquiring metal.

[0023]

According to a preferred mode of the present invention, the film contains an anti-bacterial metal.

[0024]

According to a preferred mode of the present invention, the film contains silver.

[0025]

According to a preferred mode of the present invention, the substrate is a glass or a mirror containing an

alkali-modified ingredient, and the intermediate layer is a layer to prevent diffusion of the alkali-modified ingredient.

[0026]

According to a preferred mode of the present invention, the layer to prevent diffusion of the alkali-modified ingredient is a high purity silica layer.

[0027]

According to a preferred mode of the present invention, the layer to prevent diffusion of the alkali-modified ingredient is a layer containing an electron-acquiring metal.

[0028]

According to a preferred mode of the present invention, the surface layer is made of a hydrophilicized photo-resistant resin and a photocatalyst, and the intermediate layer is a basecoat layer made of a resin.

[0029]

According to a preferred mode of the present invention, the film made of a hydrophilic material made of a hydrophilicized photo-resistant resin.

[0030]

According to a preferred mode of the present invention, a part of heat-generating means is added to the surface layer.

[0031]

According to a preferred mode of the present invention, a part of the heat-generating means is added to the film.

[0032]

According to a preferred mode of the present invention,

a part of the heat-generating means is a tin oxide transparent electrode to which a means for impressing voltage is connected.

[0033]

According to a preferred mode of the present invention, a translucent member comprises a plurality of translucent materials laminated to each other, wherein the surface layer forming the uppermost surface of the laminated materials has a hydrophilic exposed surface and a means for sustaining the hydrophilicity, and wherein a gap is formed between at least a pair of the laminated materials.

[0034]

According to a preferred mode of the present invention, a translucent member comprises a plurality of translucent materials laminated to each other, wherein the surface layer forming the uppermost surface of the laminated materials has a hydrophilic exposed surface, a means for sustaining the hydrophilicity, and a part of heat-generating means, and wherein a gap is formed between at least a pair of the laminated materials.

[0035]

According to a preferred mode of the present invention, a translucent member comprises a plurality of materials laminated to each other, wherein the surface layer forming the uppermost surface of the laminated materials has a hydrophilic exposed surface, means for sustaining the hydrophilicity, and a tin oxide translucent electrode, and wherein a gap is formed between at least a pair of the laminated materials, and wherein the electrode is connected with a means for impressing voltage thereto.

[0036]

According to a preferred mode of the present invention, a means for irradiating ultraviolet light is located at periphery of the translucent member.

[0037]

According to a preferred mode of the present invention, a rim section is located to enclose the means for irradiating ultraviolet light.

[0038]

According to a preferred mode of the present invention, the rim section is made by a reflection plate.

[0039]

According to a preferred mode of the present invention, a translucent member comprises a plurality of translucent materials laminated to each other, wherein the surface layer forming the uppermost surface of laminated materials has a hydrophilic exposed surface of the laminated materials and a means for sustaining the hydrophilicity, and wherein a means for irradiating ultraviolet light is located between at least a pair of the laminated materials.

[0040]

According to a preferred mode of the present invention, a means for irradiating ultraviolet light is located at rear face of the translucent member.

[0041]

According to a preferred mode of the present invention, the translucent member is a mirror.

[0042]

According to a preferred mode of the present invention, the translucent member is a mirror in bathroom or in

lavatory.

[0043]

The present invention provides a method for manufacturing antifogging translucent member comprising a hydrophilic film containing a photocatalyst, which method comprises the steps of: preparing a liquid by mixing a photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure the liquid by pouring thereof into a mold; separating thus formed shape from the mold; then irradiating light containing ultraviolet light to the shape.

[0044]

The present invention provides a method for manufacturing antifogging translucent member comprising a hydrophilic film containing a photocatalyst and an anti-bacterial metal, which method comprises the steps of: mixing a photocatalyst sol with a solution containing an anti-bacterial metal ion; preparing a liquid by mixing the solution of photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure the liquid by pouring thereof into a mold; separating thus formed shape from the mold; then irradiating light containing ultraviolet light to the shape.

[0045]

The present invention provides a method for manufacturing antifogging translucent member comprising a hydrophilic film containing a photocatalyst and an anti-bacterial metal, which method comprises the steps of: mixing a photocatalyst sol with a solution containing an anti-bacterial metal ion; irradiating light containing

ultraviolet light to the photocatalyst sol solution; preparing a liquid by mixing the solution of irradiated photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure the liquid by pouring thereof into a mold; separating thus formed shape from the mold; then irradiating light containing ultraviolet light to the shape.

[0046]

The present invention provides a method for manufacturing antifogging translucent member comprising a hydrophilic film containing a photocatalyst and an anti-bacterial metal, which method comprises the steps of: preparing a liquid by mixing a photocatalyst sol with a thermosetting resin having a photo-resistant ingredient in backbone thereof; heating to cure the liquid by pouring thereof into a mold; separating thus formed shape from the mold; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light containing ultraviolet light to the shape.

[0047]

The present invention provides a method for manufacturing antifogging translucent member comprising a hydrophilic film containing a photocatalyst, which method comprises the steps of: applying photocatalytic particles onto the surface of an injection molding die; conducting injection molding within the injection molding die using a compound of thermoplastic resin having a photo-resistant ingredient in backbone thereof; then irradiating light containing ultraviolet light to thus molded shape.

[0048]

The present invention provides a method for manufacturing antifogging translucent member comprising a hydrophilic film containing a photocatalyst, which method comprises the steps of: preparing mixed particles by fixing an anti-bacterial metal to photocatalytic particles; applying the mixed particles onto the surface of an injection molding die; conducting injection molding within the injection molding die using a compound of thermoplastic resin having a photo-resistant ingredient in backbone thereof; then irradiating light containing ultraviolet light to thus molded shape.

[0049]

The present invention provides a method for manufacturing antifogging translucent member comprising a glass substrate and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: applying a precursor of photocatalyst onto the surface of the glass substrate; then firing the applied glass substrate.

[0050]

The present invention provides a method for manufacturing antifogging translucent member comprising a glass substrate containing an alkali metal or an alkali earth metal, and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto a glass substrate containing an alkali metal or an alkali earth metal; applying a precursor of photocatalyst onto the surface of the glass substrate; then firing the applied glass substrate.

[0051]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; then applying silver onto rear face of the glass using the silver mirror reaction.

[0052]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; applying silver onto rear face of the glass using the silver mirror reaction; then protecting thus formed silver mirror section using a resin composition or the like.

[0053]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; then applying silver onto rear face of the glass using the silver mirror reaction.

[0054]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto a glass substrate before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; applying silver onto rear face of the glass using the silver mirror reaction; then protecting thus formed silver mirror section using a resin composition or the like.

[0055]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: after fabricating the mirror, applying a precursor of photocatalyst onto the surface of the mirror; then firing the applied mirror.

[0056]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst, which method comprises the steps of: after fabricating the mirror, forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of the mirror; applying a precursor of photocatalyst onto the glass layer; then firing the applied mirror.

[0057]

The present invention provides a method for manufacturing antifogging translucent member comprising a glass substrate, and surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: applying a precursor of photocatalyst onto the surface of the glass substrate; firing the applied glass substrate; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; then irradiating light including ultraviolet light to the shape.

[0058]

The present invention provides a method for manufacturing antifogging translucent member comprising a glass substrate, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of the glass substrate; applying a precursor of photocatalyst onto the glass substrate, firing the applied glass layer; applying a solution containing an anti-bacterial metal ion onto the surface of the layer of applied precursor of photocatalyst; then irradiating light including ultraviolet light to thus fired shape.

[0059]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: applying a precursor of

photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of the fired shape; irradiating light including ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

[0060]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; irradiating light including ultraviolet light to the shape; fixing silver onto rear face of the shape using the silver mirror reaction; then protecting thus formed silver mirror section with a resin composition or the like.

[0061]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; fixing silver onto rear face of thus fired shape using the silver mirror reaction; applying a solution containing an anti-bacterial

metal ion onto the surface of the shape; then irradiating light including ultraviolet light to the shape.

[0062]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: applying a precursor of photocatalyst onto the surface of a glass before fabricating the mirror; firing the applied glass; fixing silver onto rear face of thus fired shape using the silver mirror reaction; protecting thus formed silver mirror section with a resin composition or the like; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light including ultraviolet light to the shape.

[0063]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: after fabricating the mirror, applying a precursor of photocatalyst onto the surface of the mirror; firing the applied mirror; applying a solution containing an anti-bacterial metal ion onto the surface of the fired mirror; then irradiating light including ultraviolet light to the mirror.

[0064]

The present invention provides a method for manufacturing antifogging translucent member comprising a

mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; irradiating light including ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

[0065]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; irradiating light containing ultraviolet light to the shape; fixing silver onto rear face of thus fired shape using the silver mirror reaction; then protecting thus formed silver mirror section using a resin composition and the like.

[0066]

The present invention provides a method for manufacturing antifogging translucent member comprising a

mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; fixing silver onto the rear face of thus fired shape using the silver mirror reaction; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light including ultraviolet light to the shape.

[0067]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic photocatalyst and an anti-bacterial metal, which method comprises the steps of: forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of a glass before fabricating the mirror; applying a precursor of photocatalyst onto the glass layer; firing the applied glass; fixing silver onto rear face of the glass using the silver mirror reaction; protecting thus formed silver mirror section by a resin composition or the like; applying a solution containing an anti-bacterial metal ion onto the protective resin layer; then irradiating light containing ultraviolet light against the applied glass.

[0068]

The present invention provides a method for manufacturing antifogging translucent member comprising a mirror, and a surface layer made of a hydrophilic

photocatalyst and an anti-bacterial metal, which method comprises the steps of: after fabricating the mirror, forming a glass layer containing no alkali metal nor alkali earth metal onto the surface of the mirror; applying a precursor of photocatalyst onto the surface of the glass layer; firing the applied glass; applying a solution containing an anti-bacterial metal ion onto the surface of thus fired shape; then irradiating light including ultraviolet light to the shape.

[0069]

According to a preferred mode of the present invention, the step for applying precursor of photocatalyst onto the surface of a substrate comprises the steps of: preparing an applying liquid by adding a diluent and a hydrolysis suppressor to alkoxide which is a precursor of photocatalyst; then applying the prepared liquid onto the surface of the glass substrate.

[0070]

According to a preferred mode of the present invention, the step for forming a glass layer containing no alkali metal nor alkali earth metal is a step for applying a precursor of silicon glass onto the surface of a glass substrate.

[0071]

According to a preferred mode of the present invention, the step for forming a glass layer containing no alkali metal nor alkali earth metal comprises the steps of: preparing an applying liquid by adding a diluent, water, and a hydrolysis suppressor to alkoxide which is a precursor of silicon glass; then applying thus prepared liquid onto the

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surface of a glass substrate.

[0072]

According to a preferred mode of the present invention, the step for applying the applying liquid onto the surface of a substrate is conducted using dry air.

[0073]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting a hydrophilic photocatalyst and a hydrophilic material, which method comprises the steps of: preparing a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin; applying thus prepared liquid onto the surface of the substrate; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

[0074]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprises the steps of: forming a basecoat layer onto the surface of the substrate; applying liquid containing a photocatalyst and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

[0075]

The present invention provides a method for manufacturing antifogging translucent member comprising a

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substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of; mixing a photocatalyst sol and a solution containing an anti-bacterial metal ion; preparing a liquid by adding a photo-resistant thermosetting resin to the solution; applying the liquid onto the basecoat layer; heating to cure the applied liquid; then irradiating light containing ultraviolet light to the cured shape.

[0076]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of; forming a basecoat layer onto the surface of the substrate; mixing a photocatalyst sol and a solution containing an anti-bacterial metal ion; preparing a liquid by adding a photo-resistant thermosetting resin to the solution; applying the liquid onto the surface of the substrate; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

[0077]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: preparing a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin; applying the liquid onto the surface of

the substrate; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

[0078]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and hydrophilic material, which method comprises the steps of: forming a basecoat layer onto the surface of the substrate; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of the basecoat layer; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

[0079]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprises the steps of; after fabricating a mirror, applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of the mirror; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

[0080]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic

photocatalyst and a hydrophilic material, which method comprises the steps of: after fabricating a mirror, forming a basecoat layer onto the surface of the mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

[0081]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprises the steps of: applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror, heating to cure the applied liquid; irradiating light containing ultraviolet light to thus cured shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

[0082]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprises the steps of: forming a basecoat layer onto the surface of glass before fabricating a mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; irradiating light containing ultraviolet light to thus cured shape; then fixing silver onto rear face

of the shape using the silver mirror reaction.

[0083]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprises the steps of: applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror; heating to cure the applied liquid; fixing silver onto rear face of thus cured shape using the silver mirror reaction; then irradiating light containing ultraviolet light to the shape.

[0084]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material, which method comprises the steps of: forming a basecoat layer onto the surface of a glass before fabricating a mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; fixing silver onto rear face of thus cured shape using the silver mirror reaction; then irradiating light containing ultraviolet light to the shape.

[0085]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial -

metal, which method comprises the steps of: after fabricating a mirror, mixing a photocatalyst sol with a solution containing anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixed solution; applying thus prepared solution onto the surface of the mirror; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

[0086]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: after fabricating a mirror, forming a basecoat layer on the surface of the mirror; mixing a photocatalyst sol with a solution containing anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixed solution; applying thus prepared liquid onto the basecoat layer; heating to cure the applied liquid; then irradiating light containing ultraviolet light to thus cured shape.

[0087]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: after fabricating a mirror, applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of the mirror; heating to cure the applied liquid; applying a solution containing an anti-bacterial

metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

[0088]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: after fabricating a mirror, forming a basecoat layer on the mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; then irradiating light containing ultraviolet light to the shape.

[0089]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: mixing a photocatalyst sol with a solution containing an anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixture; applying thus prepared solution onto the surface of a glass before fabricating a mirror; heating to cure the applied solution; irradiating light containing ultraviolet light to the cured shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

[0090]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: forming a basecoat layer on the surface of a glass before fabricating a mirror; mixing a photocatalyst sol with a solution containing an anti-bacterial metal ion; adding a photo-resistant thermosetting resin to the mixture; applying thus prepared solution onto the surface of the basecoat layer; heating to cure the applied solution; irradiating light containing ultraviolet light to thus cured shape; then fixing silver onto the rear face of the shape using the silver mirror reaction.

[0091]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; irradiating light containing ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

[0092]

The present invention provides a method for

manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of; forming a basecoat layer onto the surface of a glass before fabricating a mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; applying a solution containing an anti-bacterial metal ion onto thus cured shape; irradiating light containing ultraviolet light to the shape; then fixing silver onto rear face of the shape using the silver mirror reaction.

[0093]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the surface of a glass before fabricating a mirror; heating to cure the applied liquid; fixing silver onto rear face of thus cured shape using the silver mirror reaction; applying a solution containing an anti-bacterial metal ion onto the surface of the shape; then irradiating light containing ultraviolet light to the shape.

[0094]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer consisting of a hydrophilic

photocatalyst, a hydrophilic material, and an anti-bacterial metal, which method comprises the steps of: forming a basecoat layer onto the surface of a glass before fabricating a mirror; applying a liquid containing a photocatalyst sol and a photo-resistant thermosetting resin onto the basecoat layer; heating to cure the applied liquid; fixing silver onto the rear face of thus cured shape using the silver mirror reaction; applying a solution containing an anti-bacterial metal ion onto the shape; then irradiating light containing ultraviolet light to the shape.

[0095]

According to a preferred mode of the present invention, a drying step is inserted after completing the step for forming the basecoat layer.

[0096]

According to a preferred mode of the present invention, an antifogging translucent film made of a hydrophilic material containing a photocatalyst is attached to the substrate.

[0097]

According to a preferred mode of the present invention, an antifogging translucent film made of a hydrophilic material containing a photocatalyst is attached to the substrate via a binder.

[0098]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material, while exposed surface being consisted only of the hydrophilic material, which method comprises the

steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; then firing the shape again.

[0099]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; applying an amorphous material onto the applied photocatalyst sol; then firing the applied substrate.

[0100]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a mixed solution of a photocatalyst sol and an anti-bacterial metal ion onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; then firing again the applied substrate.

[0101]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while

exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a mixture of a photocatalyst sol and a solution containing an anti-bacterial metal ion onto the surface of the substrate; applying an amorphous material onto the applied mixed solution; then firing the applied substrate.

[0102]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; firing the applied shape again; applying a solution containing an anti-bacterial metal ion onto thus re-fired shape; then irradiating light containing ultraviolet light to the shape.

[0103]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; applying an amorphous material onto the photocatalyst sol layer; firing the applied substrate; applying a solution containing an anti-bacterial metal ion onto thus re-fired

shape; then irradiating light containing ultraviolet light to the shape.

[0104]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying an amorphous material onto thus fired shape; applying a solution containing an anti-bacterial metal ion onto the applied amorphous material; then firing the substrate again.

[0105]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; applying an amorphous material onto the applied sol layer; applying a solution containing an anti-bacterial metallic ion onto the applied amorphous material; then firing the substrate.

[0106]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a

hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; applying a solution containing an anti-bacterial metallic ion onto the applied photocatalyst sol layer; applying an amorphous material onto the applied anti-bacterial ion layer; then firing the substrate.

[0107]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made of a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; firing the applied substrate; applying a solution containing an anti-bacterial metallic ion onto thus fired shape; applying an amorphous material onto the applied anti-bacterial metallic ion layer; then firing the substrate again.

[0108]

The present invention provides a method for manufacturing antifogging translucent member comprising a substrate, and a surface layer made a photocatalyst, a hydrophilic material, and an anti-bacterial metal, while exposed surface being consisted only of the hydrophilic material, which method comprises the steps of: applying a photocatalyst sol onto the surface of the substrate; applying solution containing an anti-bacterial metallic ion onto the applied photocatalyst sol layer; firing the applied

substrate; applying an amorphous material onto thus fired shape; then firing the substrate again.

[0109]

The present invention provides a method for preventing fogging of a translucent member, which method comprising: supplying dry air against the surface of the translucent member having a hydrophilic exposed surface and having a means to sustain hydrophilicity.

[0110]

The present invention provides a method for preventing fogging of a translucent member, which method comprising: irradiating ultraviolet light against the surface of the translucent member having a hydrophilic exposed surface and having a means to sustain hydrophilicity.

[0111]

[Constituent of the Invention]

Regarding the translucent member, the antifogging function is provided owing to the presence of a hydrophilic exposed surface and a means to sustain the hydrophilic exposed surface according to the mechanism described below.

Fogging on the surface of member appears when water vapor molecules having a vapor pressure above the saturation pressure are generated within an enclosed space, and when the supersaturated water vapor molecules are rejected from the enclosed space to condensate onto the wall surface and floor surface, thus growing to water droplets.

Appearance of the condensed waver vapor molecules differs with the size of droplets. When the wave length of light is expressed by ramda, the most significant fogging is observed when the droplet size is about half of ramade. The

reason is that the scattering efficiency of light becomes highest when the droplet size is about half of ramda.

[0112]

Accordingly, in the case of glass, for example, light passes through the glass with very little scattering if no droplet exists on the glass surface, so an observer inside of the enclosed space identifies that the glass is transparent. If, however, droplets appeared on the glass surface, and if the droplets grew to about half of ramda, light is scattered by the droplets, and the scattered light reaches the eyes of the observer, thus letting the observer identify fogging.

For the case of mirror, if there is no droplets on the mirror, the image reflected on the silver mirror section at rear face of the mirror reaches the eyes of the observer. If however, droplets appeared on the mirror, and if the droplets grew to a size of about half ramda, then the incident light and reflected light scatter owing to the droplets, thus generating contrast on the image, and fogging is observed.

[0113]

Therefore, no fogging appears when the surface of member is improved not to increase the droplet size to about half of ramda.

When the surface of the member is modified to hydrophilic, although water vapor molecules attach the surface of the material, the growing speed of the attached water vapor molecules is rapid, and they readily spread in film state so that no water droplet is formed and that no scattering of light appears, thus no fogging occurs.

To bring the surface of the member to hydrophilic, the member surface may be structured by a hydrophilic material. Typical hydrophilic materials include glass, polyamide, polyvinylidene fluoride.

[0114]

Glass shows a good hydrophilicity as-manufactured state showing about 5 to about 20 degrees of contact angle with water. When time elapsed, however, ingredients such as lower carboxylic acids or the like which contain both hydrophilic group and hydrophobic group gradually adsorb onto the glass surface, thus bringing the surface hydrophobic ("Glass Surface Design", Kindai Henshusha, Co., 1983). Accordingly, when water vapor molecules attach to the surface of material, they grow to water droplets. As a result, fogging likely occurs. In principle, polyamide and polyvinylidene fluoride induce similar phenomenon with the case of lower carboxylic acids to likely induce fogging.

Furthermore, polyamide and polyvinylidene fluoride have a disadvantage of soft and weak strength of film.

Conclusively, when the member surface is structured solely with a hydrophilic material, it is difficult to sustain antifogging performance for a long period.

[0115]

To this point, if a means to sustain the hydrophilic exposed surface is added, the above-described surface hydrophobic phenomenon does not appear. With the means, attached water vapor molecules on the material surface are effectively prevented from changing the property of member surface such as property to grow into water droplets, thus ensuring the prolonged antifogging performance.

[0116]

By adding a surface layer provided with a hydrophilic exposed surface and a means to sustain the hydrophilic exposed surface, antifogging function is favorably provided on the surface of various kinds of substrates.

[0117]

When the means for sustaining the hydrophilic exposed surface is a photocatalyst, only irradiation of sun light and lighting which contain ultraviolet light induces decomposition of the above-described ingredients so that the hydrophilicized surface is recovered. When the light including ultraviolet light is continuously irradiated, the hydrophilicized surface is sustained.

[0118]

If the size of particles and micropores in the surface layer is limited to 0.2 microns or less, no translucent performance is lost caused by scattering of light even when the thickness of the surface layer exceeds the wave length of visible light. Consequently, the hydrophobicizing is advantageously and effectively prevented by adding a large amount of the means to sustain the hydrophilic exposed surface.

[0119]

By adding a photocatalyst to the film made of a hydrophilic material, the hydrophilicity is sustained for a long period only by irradiating light to the film surface. In addition, by solely irradiating light to the surface, once-lost hydrophilicity on the surface is recovered. Accordingly, the film surface sustains antifogging performance for a long period.

[0120]

By forming a surface layer consisting only of a hydrophilic photocatalyst onto the substrate surface, the substrate surface sustains the hydrophilicity for a long period only by irradiating light to the surface thereof. In addition, by solely irradiating light to the surface, once-lost hydrophilicity on the surface is recovered. Accordingly, the substrate surface sustains antifogging performance for a long period.

[0121]

By forming a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material of non-photocatalyst onto the surface of substrate, the substrate surface sustains the hydrophilicity for a long period only by irradiating light to the surface thereof. In addition, by solely irradiating light to the surface, once-lost hydrophilicity on the surface is recovered. Accordingly, the substrate surface sustains antifogging performance for a long period.

[0122]

By forming a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material of non-photocatalyst onto the surface of substrate, and by forming the exposed surface by a hydrophilic material of non-photocatalyst, the substrate surface sustains the hydrophilicity for a long period only by irradiating light to the surface thereof. In addition, by solely irradiating light to the surface, once-lost hydrophilicity on the surface is recovered. Accordingly, the substrate surface sustains antifogging performance for a long period.

[0123]

By sandwiching an intermediate layer between the substrate and the surface layer, various kinds of functions are added to the intermediate layer. For example, when a transparent electrode is located in the intermediate layer and when the electrode is connected to the power source via leads, the antifogging function on the basis of heat-generating means is simultaneously functioned.

[0124]

For an antifogging translucent member comprising a substrate and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material of non-photocatalyst, an antifogging translucent member comprising a film made of a hydrophilic material containing a photocatalyst, or an antifogging translucent member comprising a substrate and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic material of non-photocatalyst while exposed surface is made of a hydrophilic material of non-photocatalyst, if the hydrophilic material is preferably made of a hydrophilicized photo-resistant resin to allow manufacture the above-described antifogging translucent member only a simple process to mix the photocatalyst with the resin in a liquid followed by applying the mixture onto the substrate or to mold the mixture, then by treating at a low temperature ranging from ambient temperature to about 300°C using a hydrophilicized photo-resistant resin as the hydrophilic material.

[0125]

For an antifogging translucent member comprising a

substrate and a surface layer consisting of a photocatalyst and surface layer consisting of a photocatalyst and hydrophilic material of non-photocatalyst, an antifogging translucent member comprising a film made of a hydrophilic material containing a photocatalyst, or an antifogging translucent member comprising a substrate and a surface layer consisting of a hydrophilic photocatalyst and a hydrophilic non-photocatalyst while exposed surface is made of a hydrophilic material of non-photocatalyst, the hydrophilic material is preferably made of an inorganic amorphous material to acquire a hard surface to sustain the antifogging performance for a long period and to recover the antifogging performance.

[0126]

By selecting a resin having Si-O bond or Si-N bond in the backbone of the hydrophilicized photo-resistant resin, the Si-O bond or S-N bond preferably has hydrophilicity, and the silicone resins and silazane resins such as siloxane resin, chlorosilane resin having these bonds in their backbone show highest photo-resistance among resins.

[0127]

When the hydrophilicization is carried out by irradiating ultraviolet light to a position of alkyl group, which reacts with ultraviolet light, contained in a resin structured by photo-resistant ingredient at least at the backbone thereof to decompose or oxidize, a hydrophilic surface having sufficient film strength is readily formed different from the case that direct addition of hydrophilic resin such as polyamide and polyvinylfluoride to the surface of the member.

[0128]

It is preferable to add an electron-acquiring metal to the surface layer because the additive significantly improves the deodorizing function based on the photocatalyst function is added to the above-described antifogging effect.

[0129]

It is preferable to add an anti-bacterial metal to the surface layer because a synergy effect of photocatalyst function and anti-bacterial metal to provide sufficient anti-bacterial force at the surface of member, adding to the above-described antifogging effect. It is also preferable to add the anti-bacterial metal because the anti-bacterial metal is gradually released into water, which provides water with anti-bacterial property under an environment that the member is used in bathroom, lavatory, toilet, kitchen, and the like.

[0130]

It is preferable to add silver to the surface layer because the above-described anti-bacterial property is functioned without degrading the sustaining performance of hydrophilicity and recovery function of photocatalyst.

[0131]

It is preferable to add an electron-acquiring metal to a film because the deodorizing function based on the photocatalytic function is significantly improved adding to the above-described antifogging effect.

[0132]

It is preferable to add an anti-bacterial metal to a film because the synergy effect of sufficient anti-bacterial force at the surface of member adding to the above-described



D E C L A R A T I O N

In the matter of the
Application for Patent under
EPC in the name of TOTO LTD.

I, the undersigned, Kameichi Nakano, of Kyowa Patent and Law Office located at 2-3, Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, do solemnly and sincerely declare as follows:

1. I am well acquainted with the English and Japanese languages and am competent to translate from Japanese into English.
2. I have executed to the best of my ability a true and correct translation into English of the complete specification and claim(s) originally filed as Japanese Patent Application No. 205019/1995 dated July 8, 1995.

Dated this 15th day of October, 1997

Kameichi Nakano
Kameichi Nakano

7-205019

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FORMING THE SAME

Number of Claim(s): 6

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto CHIKUNI

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Atsushi KITAMURA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Toshiya WATANABE

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome,
Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto HAYAKAWA

Applicant:

Identification Number: 000010087

Postal code: 802
Address: 1-1 Nakashima 2-Chome, Kokura-Kita-Ku,
Kitakyushu-Shi, Fukuoka-Ken

Name: TOTO LTD
Representative: Shigeru Ezoe

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Specification 1

Drawing 1

Abstract 1

(Translation)

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SPECIFICATION

1. TITLE OF THE INVENTION

Outdoor member and method for forming the same

[Claims]

1. An outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material thereon.
2. An outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a modified silicone resin thereon.
3. An outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a resin in which a modified portion of a modified silicone resin is polarized.
4. An outdoor member of either one of claim 1, claim 2, and claim 3, wherein the surface layer further includes silver.
5. An outdoor member of either one of claims 1 through 4, wherein the outdoor member is a member for external walls.
6. A method for forming the member claimed in either one of claims 3 through 5, wherein a light containing ultraviolet light is irradiated to the surface of the substrate after forming the surface layer made of a photocatalyst and a silicone resin.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an outdoor member difficult to be contaminated with city-type contaminants such as combustion products, which member includes: the one for external walls of sky-scraping buildings and general structures and buildings; the one for casings of automobiles, electric cars, trains, airplanes, and ships; the one for legs of overhead bridges, footbridges, and bridges; the one for outdoor members such as signboards, fences, markings, stacks, lighthouses, guard rails, big wheels, outdoor statues, outdoor sculptures, outdoor monuments, memorials, and oil tanks. The present invention also relates to a method for forming the outdoor member.

[0002]

[Description of the Prior Art]

Black striped contamination appeared on external walls of structures and buildings comprises hydrophobic materials such as carbon black which is a combustion product (according to "Lecture bulletin of Annual Meeting of Architectural Institute of Japan, 1987"). The carbon black attaches to the surface of structures and buildings, and is carried by water flowing down on the surface to adhere to the structure surface (according to Report on Structure System, Architectural Institute of Japan, No. 404, 1989, 10)

Accordingly, a material having a hydrophobic surface is likely contaminated, and a material having a hydrophilic surface is difficult to be contaminated because hydrophobic materials such as combustion product carbon black are washed

off.

Based on the findings, application of a hydrophilic coating onto the surface of external walls of structures and buildings has become a recent preventive measures to avoid contamination in a shape of black vertical stripes on the external wall surface thereof ("Polymer" vol.44, 1995).

[0003]

On the other hand, a method for cleaning solid contamination is disclosed in Japanese Patent Laid-Open No. 51646/1995. According to the disclosure, a photo-semiconductor is supported on a surface of solid which is expected to be contaminated by attaching organic matter in air, then a light containing ultraviolet light is irradiated to the photo-semiconductor to decompose the organic matter attached to the surface of the solid.

[0004]

[Problems to be Solved by the Invention]

The method solely applying a hydrophilic coating onto external walls, however, failed to sustain the hydrophilicity for a long term. The presumable reason of failing to sustain the hydrophilicity is that materials such as lower carboxylic acid and surface active agent which have functional groups of both hydrophilic and hydrophobic properties attach to the wall surface with time, thus the coating is gradually hydrophobicized.

[0005]

As for the method of cleaning solid contamination by supporting a photo-semiconductor on the surface of solid which is expected to be contaminated by attaching organic matter in air, then by irradiating a light containing

ultraviolet light to the photo-semiconductor to decompose the organic matter attached to the surface of the solid, the decomposition of organic matter has to be performed solely by the action of photo-semiconductor, which means that the intensity of ultraviolet light needs as high as 7 mW/cm^2 . Therefore, it is impossible to clean the solid contamination solely by solar rays.

[0006]

In this respect, an object of the present invention is to provide an outdoor member that is able to prevent the occurrence of vertical black stripes on external walls of structures and buildings for a long period.

[0007]

[Means to Solve the Problems]

To solve the above-described problem, the present invention provides an outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material thereon.

[0008]

The present invention provides an outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a modified silicone resin thereon.

[0009]

According to a preferred mode of the present invention, a substrate is provided with a surface layer made of a photocatalyst and a resin in which a modified portion of a modified silicone resin is polarized.

[0010]

According to a preferred mode of the present invention, the surface layer further includes silver.

[0011]

The present invention provides a method for forming a member comprising a substrate being provided with a surface layer made of a photocatalyst and a resin in which a modified portion of a modified silicone resin is polarized, wherein a light containing ultraviolet light is irradiated to the surface of the substrate after forming the surface layer made of a photocatalyst and a silicone resin.

[0012]

[Best Mode of the Invention]

The term "outdoor member" means a member or a part of the member which is used in outdoor exposed to sun rays, which member includes: the one for external walls of sky-scraping buildings and general structures and buildings; the one for casings of automobiles, electric cars, trains, airplanes, and ships; the one for legs of overhead bridges, footbridges, and bridges; the one for outdoor members such as a signboards, fences, markings, stacks, lighthouses, guard rails, big wheels, outdoor statues, outdoor sculptures, outdoor monuments, memorials, and oil tanks.

[0013]

For an outdoor member, by forming a surface layer made of a photocatalyst and a hydrophilic material on the substrate, the effect of preventing contamination of black vertical stripes is sustained owing to the hydrophilic material for a long time. The effect is functioned by the photocatalyst and solar rays, which action is described below.

Even when materials such as lower carboxylic acid and surface active agent which have functional groups of both

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hydrophilic and hydrophobic properties onto the surface of substrate, the hydrophobic functional groups are oxidized or decomposed by ultraviolet light contained in solar rays and by photocatalyst, so the hydrophilicity is sustained. As a result, outdoor members reject the adhesion of black vertical stripe contamination comprising hydrophobic materials such as combustion product carbon black for a long time.

[0014]

The term "hydrophilic material" means a material which is compatible rather with water than with oil. In concrete terms, the material has a greater contact angle with water than that with oil such as oleic acid. That type of material is the one having a strong contribution of hydrogen bond energy and dipole energy to surface energy. Examples of that type of material are inorganic oxides, resin having lots of N-H bond, S-H bond, and O-H bond on the surface thereof.

[0015]

The term "photocatalyst" means a material which forms electron-positive hole pair under irradiation of light having energy of forbidden band width or more, and which enhances reaction directly or indirectly owing to the formed electron or positive hole. Examples of the photocatalyst are titanium oxide (anatase type, rutile type), zinc oxide, tin oxide, iron oxide, tungsten oxide, strontium oxide, di-bismuth trioxide.

[0016]

For an outdoor member, by forming a surface layer made of a photocatalyst and a modified silicone resin on the

substrate, the hydrophobic functional groups of alkyl and the like in modified silicone resin are oxidized or decomposed by irradiation of solar rays, thus forming a hydrophilic surface. Once formed hydrophilic surface sustains its hydrophilicity even when materials such as lower carboxylic acid and surface active agent which have functional groups having both hydrophilic and hydrophobic properties adsorb because photocatalyst and ultraviolet light contained in solar rays successively oxidize or decompose the hydrophobic functional groups. As a result, outdoor members reject the adhesion of black vertical stripe contamination comprising hydrophobic materials such as combustion product carbon black for a long time.

Many of modified silicone resins have excellent flexibility. These flexible resins include siloxane resin, silicone rubber, cross-linked silicone resin. With these modified silicone resins, bending is possible after forming the surface layer made of a photocatalyst and a modified silicone resin on the substrate surface. The effect cannot be expected for a silicone resin to which a surface layer made of silicone resin and photocatalyst from the beginning.

[0017]

An outdoor member, of which substrate is covered with a surface layer made of a photocatalyst and a hydrophilic material, is easily prepared by, for example, forming the surface layer made of a photocatalyst and a modified silicone resin, then polar-processing the modified section of the modified silicone resin.

The term "polar-processing" means a process to give polarity by applying hydrogen bond and the like to the

modified section of the modified silicone resin comprising hydrophobic groups. An example of that type of processing is the one to oxidize or decompose the modified section of a modified silicone resin. Irradiation of light containing ultraviolet, ozone processing, and plasma processing are preferable examples of the polar-processing.

Among these processing methods, irradiation of light containing ultraviolet light is most simple one because the presence of photocatalyst in the surface layer makes polar-processing readily performed within relatively short time even under relatively weak irradiation of ultraviolet light. Applicable light containing ultraviolet light includes solar rays, light of BLB lamp, fluorescent lamp, mercury lamp, xenon lamp, and halogen lamp.

[0018]

It is preferable to add an anti-bacterial metal such as silver, copper, and zinc to the surface layer because the preventive effect against algae, mildew, moss formation.

In particular, addition of silver is preferable because the preventive effect against algae, mildew, moss formation is expected while remaining the performance of photocatalyst to sustain hydrophilicity and remaining the recovery effect.

[0019]

[Embodiments]

The present invention is described in more detail in the following referring to experimental examples.

(Example 1)

A solution of siloxane resin containing a curing agent was applied onto an aluminum substrate (10 cm square). The substrate was treated by heat at 150°C to prepare an

intermediate member P. A liquid was prepared by: adding a siloxane resin to a nitric acid deflocculating titanium oxide sol having an average particle size of $0.01 \mu\text{m}$ to a concentration of 50 wt.% to the weight sum of the solid titanium oxide and the siloxane resin; diluting the mixture by propanol; and adding a curing agent to the mixture. Thus prepared liquid was applied onto the surface of the intermediate member P. Then the member P was treated at 150°C to obtain a specimen A. A BLB lamp light (0.5 mW/cm^2) was irradiated against the specimen A for 10 hours to obtain a specimen B. Separately, a liquid was prepared by: adding a siloxane resin to a mixture of a nitric acid deflocculating titanium oxide sol having an average particle size of $0.01 \mu\text{m}$ and an aqueous solution of silver nitrate to a concentration of 50 wt.% to the weight sum of the solid titanium oxide and the siloxane resin; diluting the mixture by propanol; and adding a curing agent to the mixture. Thus prepared liquid was applied onto the surface of a separate intermediate member P. Then the member P was treated at 150°C , to which a BLB lamp light (0.5 mW/cm^2) was irradiated for 10 hours to obtain a specimen C. The specimens A through C, the aluminum substrate, and the intermediate member P were mounted to the specimen-holding section of a device shown in a Fig. 1. The device was allowed to stand on the rooftop of a five-storied building. Then, the change of attaching state of black vertical stripe contamination and the change of hydrophilicity were observed with time. The hydrophilicity was determined by the contact angle with water.

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[0020]

The change of attaching state of black vertical stripe contamination with time was evaluated by visual observation and by the color difference at various positions in the same specimen.

Visual observation found vertical stripe contamination on the aluminum substrate and the intermediate member P after 1 week, though there was no vertical stripe contamination on the specimens A through C. On the specimen A, there was observed an irregular pattern contamination after a rain in the first day. With elapsed time, however, the surface of the specimen A was hydrophilicized by the solar ray irradiation, and succeeding rains washed off the irregular pattern contamination to give clean surface similar with that of the specimens B and C.

After 1 week has passed, the aluminum substrate and the intermediate member P showed significant contamination on their whole surface area, resulting in the increase of color difference to a range of from 1 to 4. To the contrary, the specimens A through C showed very little change in color difference after 1 week compared with original state.

For the aluminum substrate and the intermediate member P after 1 week, vertical stripe contamination was observed. Depending on the position of observation, there observed a color difference of 3 on the aluminum substrate and 1.2 on the intermediate member P. For the specimens A through C, however, no vertical stripe contamination appeared, and their color difference was within 0.1 even when the observation positions were changed.

As for the degree of hydrophilicity, the aluminum

substrate and the intermediate member P gave original value of around 60 deg. and 90 deg., 1 week respectively, and became to around 70 deg. after for both of them, or became to hydrophobic property. For the specimens B and C, however, around 3 deg. of original hydrophilicity became less than 1 deg. after 1 week. The specimen A showed around 90 deg. of original hydrophilicity, and became less than 1 deg. after 1 week.

These findings proved that an outdoor member (the specimens B and C) having a substrate and a surface layer made of a photocatalyst and a resin in which the modified section of modified silicone resin was polarized thereon does not form vertical stripe contamination because the hydrophilic surface is sustained, and that an outdoor member (the specimen A) having a substrate and a surface layer made of a photocatalyst and a modified silicone resin thereon does not form vertical stripe contamination because the surface is hydrophilicized by solar rays and because the hydrophilic surface is sustained.

[0021]

The specimen B was coated with oleic acid, and was immersed to water in a position that the surface of the member becomes horizontal. The contact angle with oleic acid was immediately increased to form droplets, which droplets were then floated. For the aluminum substrate and the intermediate member P, however, dipping them horizontally facing the surface horizontal sustained the wetted state of oleic acid. That is, when the hydrophilic surface is sustained and when the member is left outdoor, rain and the like enters between the member surface and the

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hydrophobic black vertical stripe contamination, thus making the black vertical stripe contamination difficult to adhere.

[0022]

The specimen B, the aluminum substrate, and the intermediate member P were wetted with water, and were set to the device shown in Fig. 1, which device was then allowed to stand. After 30 min, the specimen B was dried, and the aluminum substrate and the intermediate member P left water droplets thereon. The phenomenon should come from the result that the specimen B was uniformly wetted with water, thus the thick water film portion should be difficult to appear. Consequently, it was confirmed that, when the present invention is applied to an outdoor member, there is an additional advantage of quick drying of member. That kind of advantage is preferable in car-wash for prompt drying, or particularly preferable for a member of vehicle casing.

[0023]

Effect of maintaining performance of hydrophilicity and recovery of hydrophilicity was determined on the specimen B. The effect of maintaining performance of hydrophilicity was evaluated from the contact angle with water before and after the irradiation of BLB lamp light (0.5 mW/cm^2) for 1 month. Effect of recovery of hydrophilicity was determined by the change of contact angle with water with time by wiping the surface of the specimen with alcohol to increase the contact angle of the surface with water, then irradiating BLB lamp light (0.5 mW/cm^2)

Both immediately after the irradiation and after 1 month from irradiation, the contact angle with water

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remained below 1 deg., at a favorable angle, to prove the sustained effect of the hydrophilicity.

After wiping off the surface with alcohol to increase the contact angle of the surface with water, BLB lamp light (0.5 mW/cm^2) was irradiated to the surface to observe the change of contact angle with water with time. About 1 hour or irradiation recovered the contact angle with water from 30 deg. to about 1 deg.

[0024]

(Example 2)

A solution of siloxane resin containing a curing agent was applied onto an aluminum substrate (10 cm square). The substrate was treated by heat at 150°C to prepare an intermediate member P.

A liquid was prepared by: adding a siloxane resin to a nitric acid deflocculating titanium oxide sol having an average particle size of $0.01 \mu\text{m}$ to a concentration of, separately, 5 wt.%, 10 wt.%, 50 wt.%, 80 wt.%, and 95 wt.% to the weight sum of the solid titanium oxide and the siloxane resin; diluting each mixture by propanol; and adding a curing agent to each mixture. Thus prepared each liquid was applied onto the surface of separate intermediate member P. Then each member P was treated at 150°C to obtain a specimen Q.

A BLB lamp light (0.5mW/cm^2) was irradiated against the specimen Q for a specified period to obtain a specimen. The water absorption rate of the specimen was less than 1%.

For the specimen and the intermediate member Q, the relation between the lamp irradiation time and the degree of hydrophilicity, the abrasion resistance, and the surface

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hardness were determined.

[0025]

Fig. 2 shows the relation between the lamp irradiation time and the degree of hydrophilicity under a condition of changed ratio of solid titanium oxide in the surface layer to the weight sum of the solid titanium oxide and the siloxane resin. The degree of hydrophilicity was evaluated by the contact angle with water.

The intermediate member Q did not show any change in contact angle with water. For all the specimens with the rate of additional 20 wt.%, 50 wt.%, 90 wt.%, and 95 wt.%, however, the contact angle with water decreased to about 3 deg. after 200 hr of irradiation. Also for the specimen with 5 wt.% content, the contact angle with water decreased to about 10 deg. within 200 hr of irradiation. It was proved that the specimens have favorable hydrophilicity.

[0026]

Fig. 3 shows the evaluation result on abrasion resistance. A rubbing abrasion was given to the surface of each specimen using a plastics eraser, then the change of appearance was observed. The criterion of the evaluation on the anti-abrasion characteristic is given below.

◎: No change occurred after 40 cycles of traverse.

○: Flaw appeared and the surface layer was separated after traversing cycles of 10 or more and less than 40.

△: Flaw appeared and the surface layer was separated after traversing cycles of 5 or more and less than 10.

×: Flaw appeared and the surface layer was separated after less than 5 cycles of traverse.

The result was that, at or less than 95 wt.% of the

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ratio of the solid titanium oxide in the surface layer to the weight sum of the solid titanium oxide and the siloxane resin, the evaluation was (○), and that the ratio is at or less than 90 wt.%, the evaluation was (◎).

[0027]

Fig. 4 shows the result of surface hardness determination. The evaluation of surface hardness was given by the hardness of pencil to generate flaw under scratch of pencils ranging from 6B to 9H in their core hardness. The hardness was about 5B for 90 wt.% of the ratio of the solid titanium oxide in the surface layer to the weight sum of the solid titanium oxide and the siloxane resin, and the hardness increased to H for 60 wt.% of the ratio to give a significant high hardness.

[0028]

[Effect of the Invention]

An outdoor member prevents the generation of black vertical stripe contamination on external wall surface of structures and buildings for a long time by forming a surface layer made of a photocatalyst and a hydrophilic material onto the substrate.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 illustrates an outdoor test device used in an example of the present invention.

[Fig. 2]

Fig. 2 shows the relation between the irradiation time of lamp light and the degree of hydrophilicization in an example of the present invention.

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[Fig. 3]

Fig. 3 shows the relation between the amount of titanium oxide in the surface layer and the abrasion resistance in an example of the present invention.

[Fig. 4]

Fig. 4 shows the relation between the amount of titanium oxide in the surface layer and the surface hardness in an example of the present invention.

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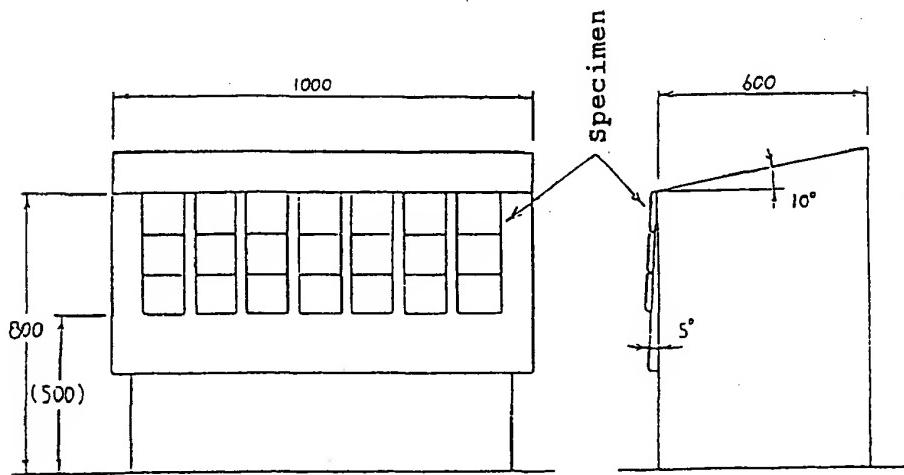
Outdoor exposed contamination test device

Fig. 1

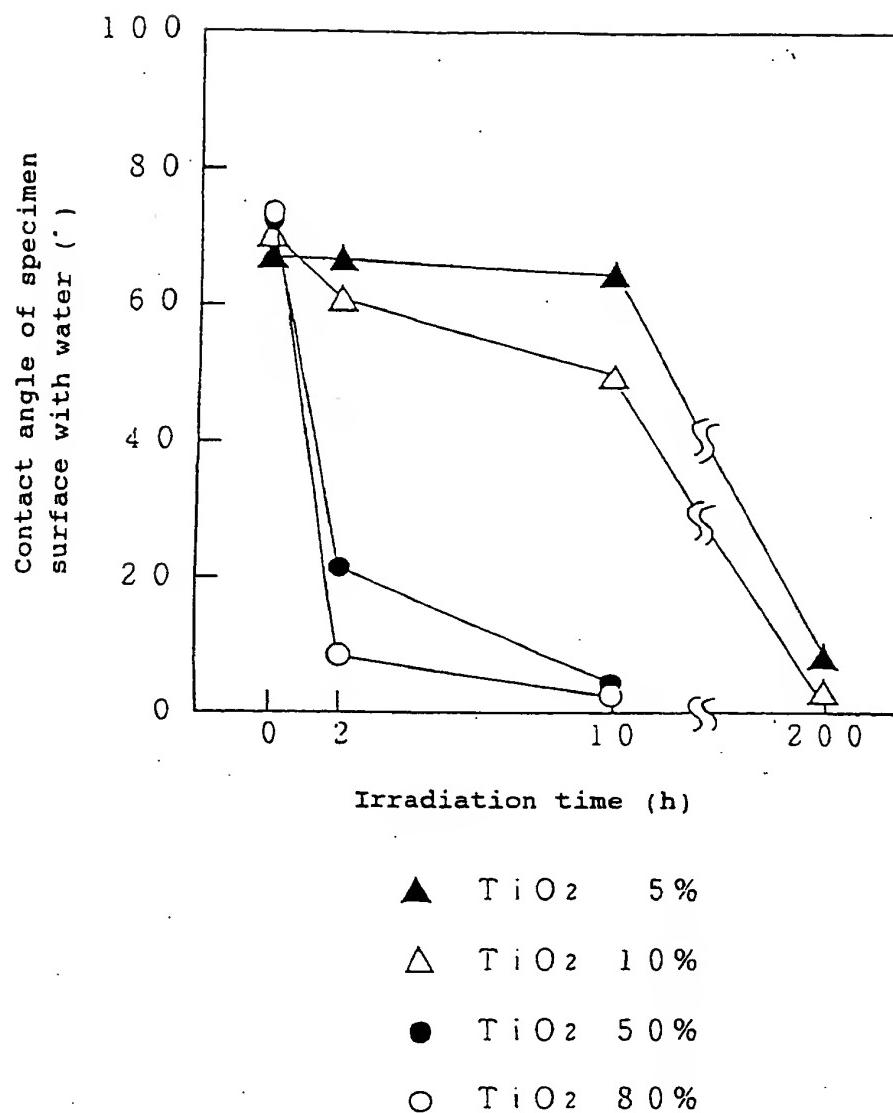


Fig. 2

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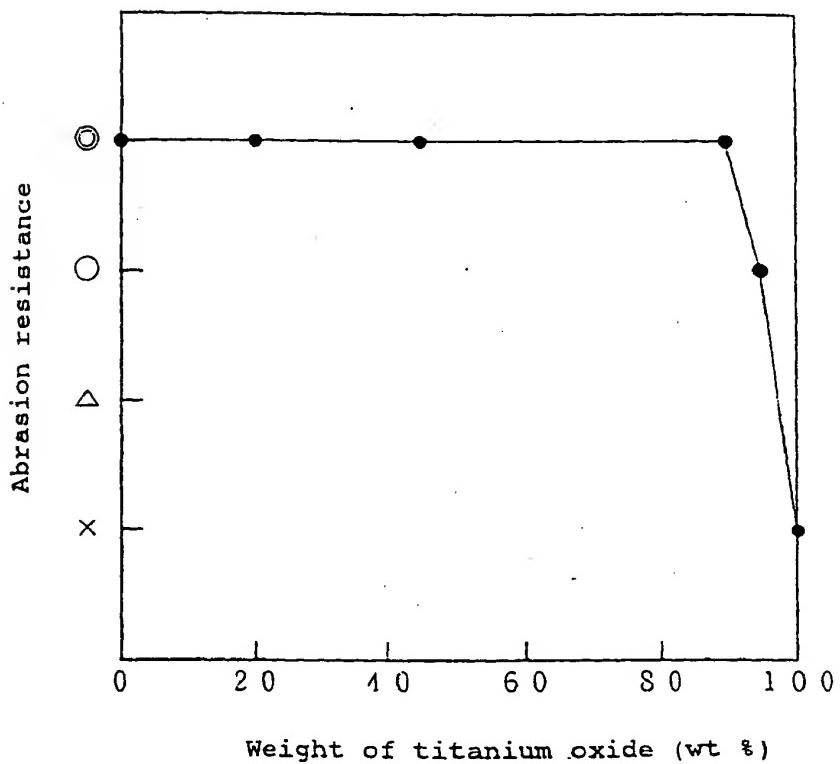


Fig. 3

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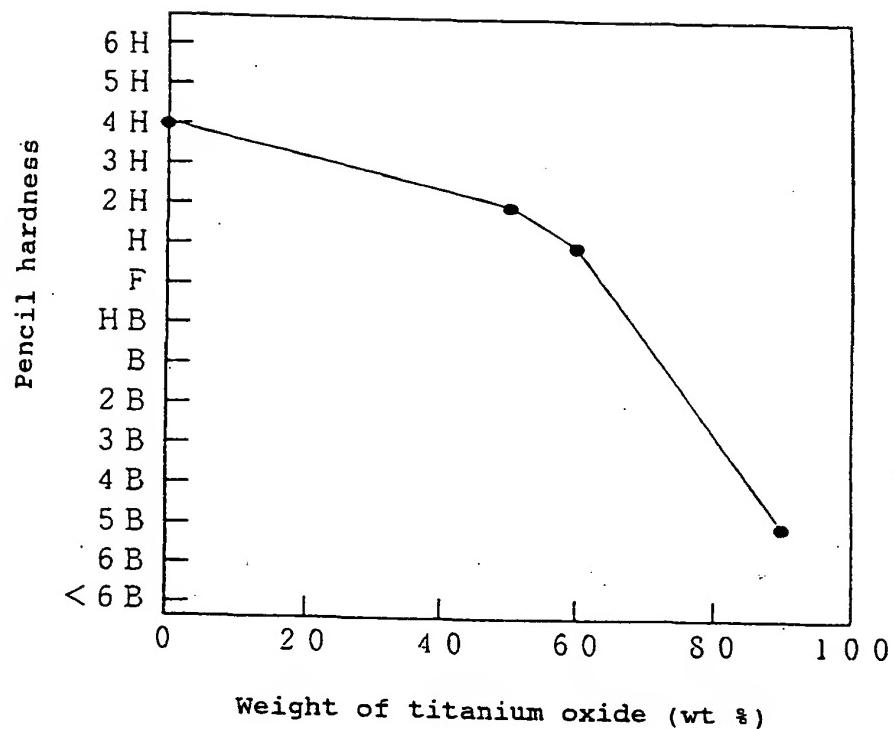


Fig. 4

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Abstract

[Object]

To provide an outdoor member to prevent generation of black vertical stripe contamination on external walls of structures and buildings for a long period.

[Conformation]

An outdoor member comprises a substrate, and a surface layer made of a photocatalyst and a hydrophilic material thereon.

[Selected Drawing]

None

